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TEKNISKA HÖGSKOLAN I LUND



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MASTER

COMPARATIVE STUDY OF
HYDROGEN AND METHANOL AS
ENERGY CARRIERS

Master Thesis in Engineering by
Anna Johansson

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DEPARTMENT OF HEAT AND POWER ENGINEERING
LUND INSTITUTE OF TECHNOLOGY
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Jämförelse av vätgas och metanol som energibärare

Referat (sammandrag)

Den här rapport har skrivits i syfte att jämföra vätgas och metanol, med bensen, som energibärare i ett framtida energisystem. Detta energisystem ska tillfredsställa kraven på hållbar utveckling. Rapporten inriktar sig på motorfordonsapplikationer.

Ett antal kriterier har utvecklats för att användas vid karakteriseringen. Kriterierna som använts i denna uppsats är utvecklade för en miljömässig jämförelse, i första hand baserad på utsläppen vid förbränning. Kriterierna följs av en kort beskrivning av vilken effekt olika indikatorer har på de enskilda kriterierna.

Vätgas kan anses som ett mycket bra alternativ till bensen och dieselolja. Vid förbränning i luft bildas endast vatten och små mängder kväveoxider. I denna rapport undersöks vätgas som producerats från förnyelsebara energikällor. Detta är nödvändigt för att uppfylla kraven på hållbar utveckling.

Metanol har många fördelar som bränsle jämfört med bensen, som till exempel lägre emissioner av kväveoxider och kolväten. Denna rapport behandlar metanol som producerats från biomassa.

Resultatet av karaktiseringen visar att vätgas kan anses som det bästa alternativet, och att även metanol visar sig vara ett bättre alternativ än bensen.

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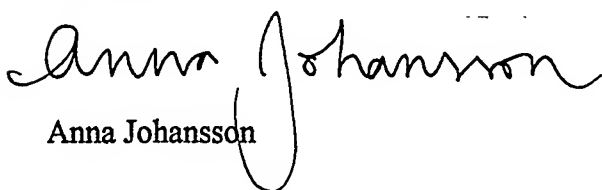
REFERNCES

Preface

This report has been written as a master thesis at Sydkraft konsult AB and the Department of Heat and Power Engineering, Lund Institute of Technology.

I wish to express my thanks to Mr. Ola Gröndalen, at Sydkraft Konsult AB, for his information, help, interest and support. I also want to thank Prof. Tord Torisson for his time and support, and a special thanks to Fredrik Olsson at the Department of Heat and Power Engineering for his help and ideas during a long time.

Malmö 980519 .

A handwritten signature in cursive script, reading "Anna Johansson". The signature is written in black ink and is positioned above the printed name.

Anna Johansson

Summary

This report has been written with the purpose to compare hydrogen and methanol, with gasoline, as energy carriers for new energy system in the future. This energy system must satisfy the demands for sustainable development. The report focuses on motor vehicle applications.

A few different criteria has been developed to help form the characterisation method. The criteria proposed in this thesis are developed for an environmental comparison mainly based on emissions from combustion. The criteria concerns the following areas

- A. Renewable resources
- B. The ozone layer
- C. The greenhouse effect
- D. The acidification
- E. Toxic substances

The criteria are followed by a short description of what effect different indicators have on that special criterion.

In many ways, hydrogen may seem as a very good alternative compared with gasoline and diesel oil. Combustion of hydrogen in air results in water (as the main product) and small amounts of oxides of nitrogen. In this report, hydrogen produced from renewable resources is investigated. This is necessary to fulfil the demands for sustainable development. Today, however, steam reforming of fossil fuels represents 99 % of the hydrogen production market. Problem areas connected with hydrogen use are for instance storage and distribution.

Methanol has many advantages, while comparing methanol and gasoline, like for instance lower emissions of oxides of nitrogen and hydrocarbons, limited emissions of carbon dioxide and no sulphur content. Methanol can be produced from many different resources, for example natural gas, naphtha, oil, coal or peat and biomass. To meet the demands for sustainable production, methanol has to be produced from biomass.

The table below shows the result of the characterisation compared with gasoline.

Fulfilment of the criterion?				
	Criteria	Hydrogen	Methanol	Gasoline
A.	The fuel should be based on renewable resources	Yes	Yes	No
B.	Should not decrease the stratospheric ozone layer, or increase the tropospheric ozone layer	No ¹	No ¹	No
C.	Greenhouse gases must not increase, but decrease	Yes	Yes	No
D.	No dispersion of emissions that contribute to the acidification	No ¹	No ¹	No
E.	Should not be a toxic hazard	Yes	No	No

¹Can be considered to be a better alternative compared with gasoline, due to lower dispersion of the listed emissions

Sammanfattning

Den här rapport har skrivits i syfte att jämföra vätgas och metanol, med bensin, som energibärare i ett framtida energisystem. Detta energisystem ska tillfredsställa kraven på hållbar utveckling. Rapporten inriktar sig på motorfordonsapplikationer.

Ett antal kriterier har utvecklats för att användas vid karakteriseringen. Kriterierna som använts i denna uppsats är utvecklade för en miljömässig jämförelse, i första hand baserad på utsläppen vid förbränning. Dessa kriterier behandlar områdena:

- A. Förnyelsebar källor
- B. Ozonskiktet
- C. Växthuseffekten
- D. Förurningen
- E. Giftiga substanser

Kriterierna följs av en kort beskrivning av vilken effekt de olika indikatorerna har på de enskilda kriterierna.

I många avseende kan vätgas anses som ett mycket bra alternativ till bensin och dieselolja. Vid förbränning av vätgas i luft bildas vatten (som huvudprodukt) och små mängder av kväveoxider. I denna rapport undersöks vätgas som producerats från förnyelsebara energikällor. För att kraven på hållbar utveckling ska kunna tillfredsställas är detta nödvändigt. I dag står dock ångreformerings av fossila bränslen för cirka 99 % av den totala vätgasproduktionen. Problemområden som dyker upp i samband med vätgasanvändning är bland annat lagring och distribution av vätgasen.

Vid jämförelse mellan metanol och bensin som bränsle visar det sig att metanol har många fördelar som till exempel lägre emissioner av kväveoxider och kolväten, begränsade koldioxidemissioner och inga svavelhalter. Metanol kan produceras från många olika källor som till exempel naturgas, nafta, olja, kol eller torv och biomassa. För att uppfylla kraven på produktion från förnyelsebara källor måste metanol produceras från biomassa.

I tabellen nedan visas resultatet av karakteriseringen.

Uppfylls kriteriet?				
	Kriterier	Hydrogen	Metanol	Bensin
A.	Bränslet ska vara baserat på förnyelsebara källor	Ja	Ja	Nej
B.	Ozonhalterna i stratosfären får inte minska, men ej heller öka i troposfären	Nej ¹	Nej ¹	Nej
C.	Mängden växthusgaser får inte öka, utan måste minska	Ja	Ja	Nej
D.	Emissioner som bidrar till förurningen får inte spridas	Nej ¹	Nej ¹	Nej
E.	Ämnet får ej vara giftigt	Ja	Nej	Nej

¹Kan antas vara ett bättre alternativ jämfört med bensin genom att utsläppen av emissioner är mindre

1. INTRODUCTION

1.1 The objective of the study

The purpose of this report is to characterise hydrogen and methanol as an energy carrier in a future sustainable energy system. The possibilities of using hydrogen or methanol as fuels for motor vehicles are being examined, and a few examples from the experimental market are presented.

I have developed a few important criteria for sustainable development, which can be related to emissions from combustion of different fuels.

The criteria are meant to be a help while studying the different fuels and making a comparison with gasoline.

1.2 Background

As the population of our world is growing rapidly, and we demand higher standard of living and even more technically advanced equipment, our already great demand for energy is increasing.

Today, the industrial countries, where about 30 % of the worlds population live, consume about 70 % of the total energy supply. We use many different primary energy resources, like for instance coal, oil and natural gas. Fossil fuels account for 85 percent of our primary energy demand [5].

While first starting to use fossil fuels for energy purpose, no one thought of the consequences. However, we are now aware of the negative things that come with the use of fossil fuels - the reserves are not infinite, and the negative impact on our environment. The reserves of oil and natural gas have been calculated to last about 40 more years [5]. The emissions of dangerous substances are constantly growing, as the population is growing as well as the energy consumption per capita.

We must find a way to meet our great energy demand in a sustainable way in an energy system where the energy sources are renewable and clean. Hydrogen can perhaps be considered as a very good alternative, and methanol is an other option.

1.3 Demarcations

To keep this report at a reasonable size, it is necessary to make some demarcations.

Sustainable development is very hard to define, because it involves such a large area. The criteria proposed in this thesis are therefore developed for an environmental comparison mainly based on emissions from combustion.

There has been no effort put in regarding economic sustainability, though it is equally important. Neither is there much effort put in considering the safety of the different methods.

The study concerns hydrogen and methanol production for end use in motor vehicle applications only. I have failed to find much information about methanol vehicles, why this part of the report is a bit short.

2. SUSTAINABLE DEVELOPMENT

2.1 Background

In 1987, the World Commission on Environment and Development (WCED) issued a report, "Our Common Future" [3], which is a global agenda for change, at the request of the General Assembly of the United Nations.

This was a signal of knowledge from the whole world, that we are endangering the future existence of life on Earth in natural balance. We are doing so by living in an unsustainable society, where the population is growing rapidly and uncontrolled, and where all kinds of resources are being used in abundance without regards for the consequences. This puts an enormous stress on the environment, and threatens millions of human lives.

In order to produce an agenda to improve these conditions, the WCED, established the concept "sustainable development" [3]

"At a minimum, sustainable development must not endanger the natural systems that support the life on Earth: the atmosphere, the waters, the soil, and the living beings."

The Intergovernmental Panel on Climate Change, IPCC, was formed in 1988. This is an international evaluation on the status of knowledge of the global climate change [20].

In June in 1992 the United Nations Conference on Environment and Development (UNCED) was held in Rio de Janeiro, and it is known as the Rio Conference [4].

It brought together representatives from 179 governments. Five documents were produced on the subject of environment and economic and social development for world-wide sustainable development.

- The Rio declaration on Environment and Development
- Agenda 21
- A statement to principles to guide the management, conservation and sustainable development of all types of forests
- The Convention on Climate Change
- The Convention on Biological Diversity

The aim of the United Nations Framework Convention on Climate Change is to stabilise greenhouse gases in the atmosphere at levels that will not dangerously upset the global climate system. This will require a reduction in our emission of such gases as carbon dioxide, a by-product from burning fuels for energy.

The Convention on Biological Diversity requires that countries adopt ways and means to conserve the variety of living species and ensure that the benefits from using biological diversity are equitably shared.

In December 1997, a new meeting with Convention on Climate Change was held in Kyoto, Japan. The ambition of the meeting was to produce a protocol for the limitation of emissions of the greenhouse gases for the industrialised countries. [20]

2.1.1 Motorism

Motorism is a word often used, which includes the use of cars as a transportation medium, but also localisation, economy, safety, environment etc. Transportation is essential for economic and social development, and the need will undoubtedly increase, but this activity is also a source of atmospheric emissions.

Pollution affects peoples and animals health and the nature around us. Globally, the pollution of greenhouse gases contributes to the greenhouse effect. Regionally, acidification of lakes and waters is a large problem. Finally, this leads to health problems on a local basis. Hence, we need to develop ways to reduce pollutant substances in the transport sector.

The number of cars per inhabitant increases all the time, and therefor also the use of fuel. Besides this, we have sea and air traffic where the usage of fuel is very large and also growing.

In 1945, Sweden had about 50 000 passenger cars, which equals one car per every 133 inhabitants [1]. The number of passenger cars increased rapidly, and in 1996 Sweden had about 3 600 000 registered passenger cars, equivalent to one car per every 2.4 inhabitants [2].

Motorism has developed very fast and is now very important for our society. About 10 % of the Swedish working population is depending on the car industry [1].

There are different exhaust regulations in different countries. In Sweden three environmental classes have been introduced for passenger cars produced from the year 1993.

	Environmental class		
	1	2	3
NO _x (g/fkm)	0.25	0.25	0.62
HC (g/fkm)	0.078	0.16	-
CO (g/fkm)	2.1	2.1	2.1

Table 1.1 *Exhaust regulation values for Sweden*

In the United States, similar exhaust regulation exists. California has a plan for the introduction of zero emission vehicles. The vehicles are divided into the following classes: TLEV- Transitional Low Emission Vehicle, LEV - Low Emission Vehicle, ULEV - Ultra Low Emission Vehicle and ZEV - Zero Emission Vehicle [21].

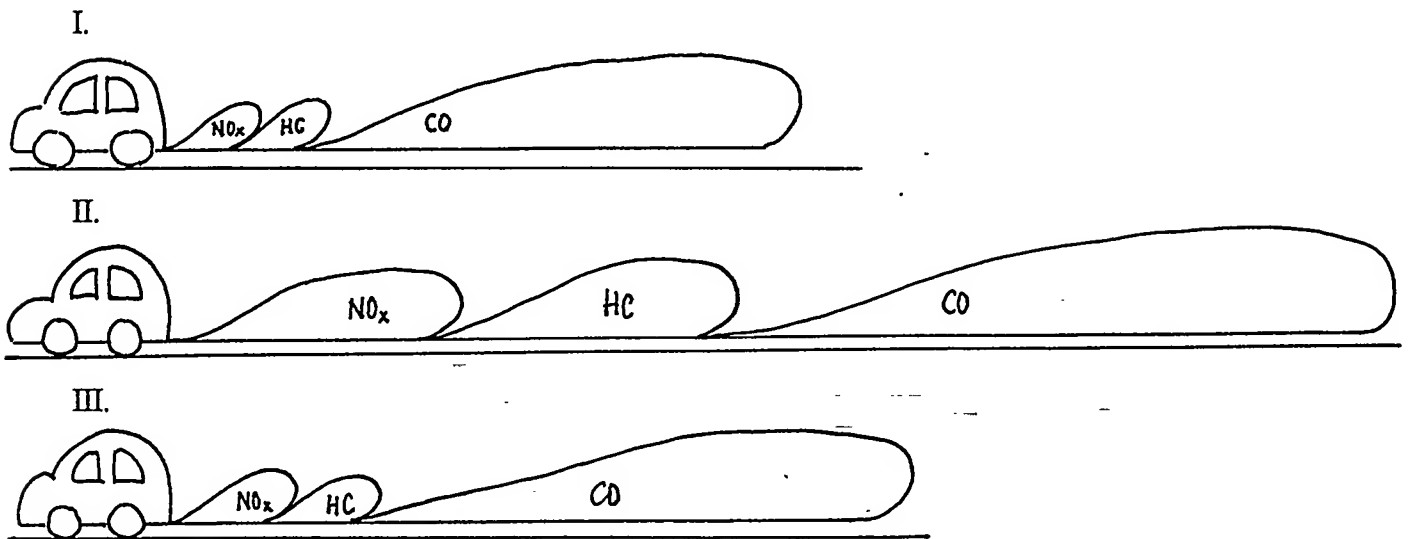
	TLEV	LEV	ULEV	ZEV
NO_x (g/fkm)	0.25	0.12	0.12	0
HC (g/fkm)	0.078	0.047	0.025	0
CO (g/fkm)	2.1	2.1	1.06	0

Table 1.2 *Exhaust regulation values for California [21]*

The current values for California, EC and Sweden are shown in table 1.3, followed by figure 1.1 for easy visual comparison.

	California		EC	Sweden	
	1989-93	93/95/97	1992/93	1989	1995
NO_x	0.25	0.124	0.97	0.62	0.25
HC	0.25/0.62	0.155	0.97	0.25	0.19/0.24
CO	4.3	2.11	2.72	2.1	2.1/2.6
Particles	0.05		0.19	0.124	0.05

Table 1.3 *Allowed exhaust values (g/km) [1]*



- I. California – 93/95/97
- II. EC
- III. Sweden - 1995

Figure 1.1 *Estimated values of CO, HC and NO_x in exhaust gases from cars [1]*

Almost all new motor vehicles in the western world these days have three-way catalytic exhaust devices, preventing the vehicles from emitting large amounts of NO_x, CO and HC.

However, using a catalytic exhaust device only reduces a part of the problem.

The catalyst oxidizes the carbon monoxide to carbon dioxide, the hydro carbons to water vapour and carbon dioxide, and reduces the nitric oxide to nitrogen and carbon dioxide. Consequently, the amount of hydro carbons and nitric oxide is reduced, but the amount of carbon dioxide is increasing.

2.2 Principles and Indicators

In this section, a few important principles and criteria for sustainable development are given.

There are many ways to choose principles, criteria and indicators, but this investigation is focused on our health and environment (ecological sustainability).

The introduction of the criteria is followed by a discussion to understand why the criteria are important. There is also a brief description of the different indicators.

Figure 2.1 shows the connection between the different chosen principles and indicators.

2.2.1 Principles

A. Non-renewable resources

Criteria: *The fuel should be based on renewable resources only.*

Indicators: *No use of fossil fuels in production, storage, distribution or utilisation.*

Energy resources are mainly divided into two different groups: non-renewable and renewable resources.

The first group consists of oil, coal, natural gas and nuclear power, while we in the later one find solar, tidal, wind and wave energy, and wood, plants, hydro power and geothermal sources.

Today's energy system is very much based on fossil fuels as energy carrier. Fossil hydro carbons-coal, oil and natural gas are being used to meet about 85 per cent of the world's energy demand [5].

Fossil fuels are, however, not considered as "sustainable fuels", since they pollute and contributes to the greenhouse effect, and further more, the resources are limited and new fuels would take millions of years to be formed.

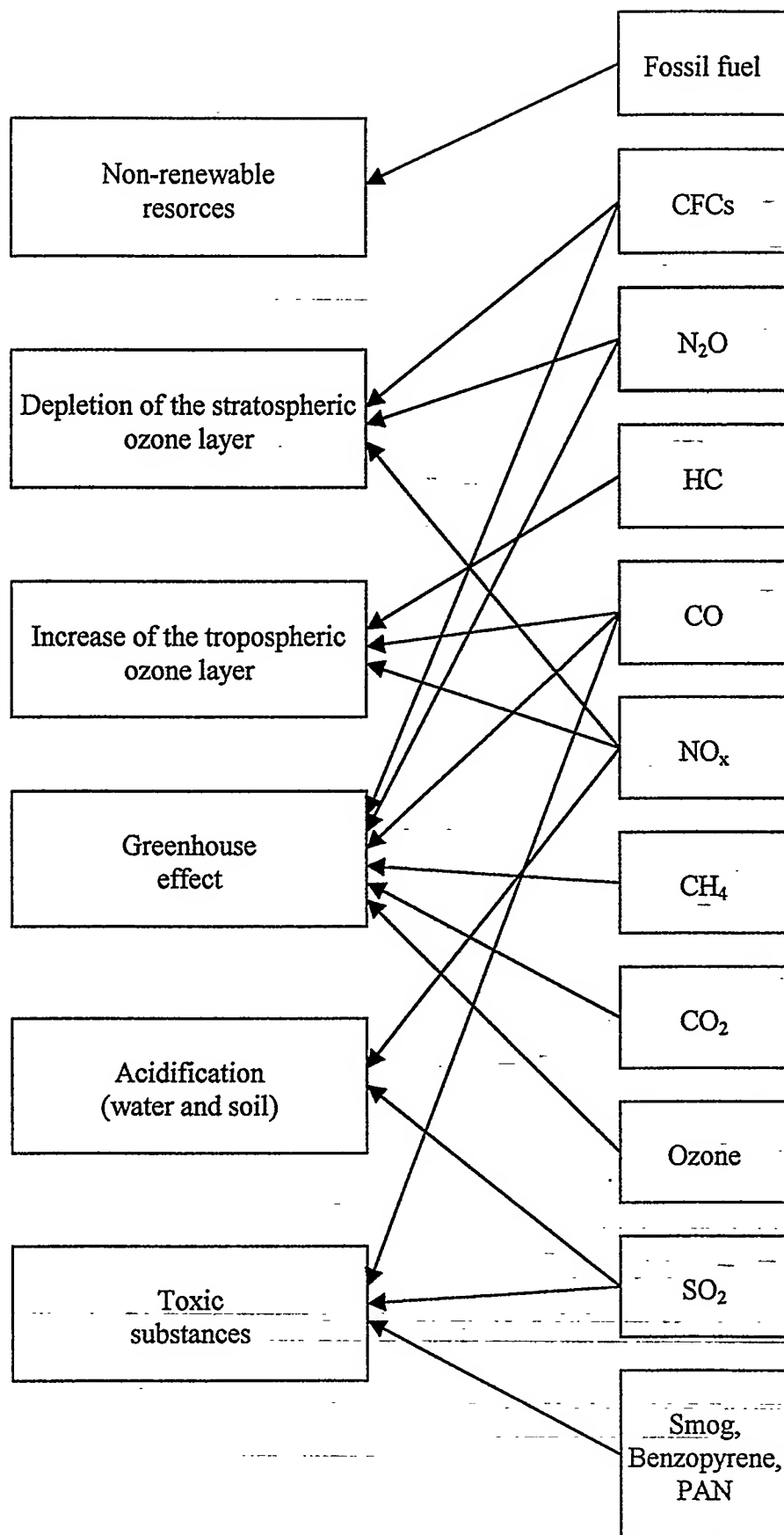


Figure 2.1 *Principles (to the left) and indicators (to the right)*

B. Ozone layer

Criteria: a) *Emissions of substances which contributes to the depletion of the stratospheric ozone layer must be minimised.*
b) *Neither should the tropospheric ozone concentration increase.*

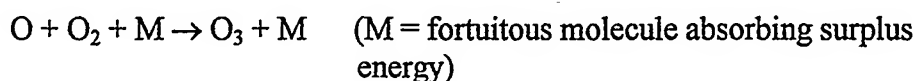
Indicators: a) N_2O , NO_x , CFCs [6]
b) HC, CO, NO_x [5][6]

Ozone, O_3 , is an allotrope modification of oxygen, and occurs everywhere in the atmosphere. The ozone is of great importance to the atmosphere's temperature relationship, and is crucial for all life on Earth.

The ozone is formed when ultraviolet rays split an "ordinary" oxygen molecule.



These are chemically active and reacts with oxygen molecules to form ozone molecules.



The ozone takes care of all sunlight with a wavelength less than 300 nm, that is it prevents the short waved part of the ultraviolet sunlight to reach the ground. Thus, only a small part of the ultraviolet radiation reaches us. Increasing the ultraviolet radiation, that is reducing the ozone layer, slows down the photosynthesis and nutrition will not be produced and we will have an obstruction of life, both human and amongst animals and all growing things. The human cost will be increased numbers of skin cancer victims[6][7].

Catalysts which affects the stratospheric ozone layer

- nitric oxide
- nitrous oxides
- chlorofluorocarbons (CFCs)

CFCs are probably the worst enemy to the ozone layer. But, since combustion of different fuels do not emit CFCs, there will be no further discussion of these substances here. Though, it is worth mentioning that for many vehicles CFCs are very often used for comfort air conditioning.

Ever since scientists discovered the hole in the ozone layer, we have been aware of the huge problem with ozone depleting gases, and the climate change following from those emissions. The energy is now used more rational and efficient, but the worlds consumption of energy and material is constantly growing. The result is that the emissions per energy-volume unit is now less than it was some ten years ago. However, we have failed to make a substantial reduction of the total emissions.

In the troposphere, the concentration of ozone is increasing. Estimated values shows that the ozone concentration has doubled since the late 1800s. The tropospheric ozone has a major

impact on climate change through global warming, and is considered to be a secondary pollutant [5].

C. Greenhouse effect

Criteria: *Emissions of "greenhouse gases" must be minimised, so that we will not risk to disturb the Earth's energy balance. At least, there must be no increase of those gases, and we should aim for a reduction of 60-80 % of today's emissions until 2050 [20]*

Indicators: *CO₂, CH₄, CO, HC, CFC, tropospheric ozone, water vapour [5][6]*

The primary greenhouse gases in the Earth's atmosphere are carbon dioxide, methane, carbon monoxide, hydrocarbons, chlorofluorocarbons (CFCs), as well as water vapour and ozone [6].

The danger of these greenhouse gases, is the fact that they are transparent. This means they let the high temperature radiation (sunlight) from the sun pass through the atmosphere to the Earth, and because of the carbon dioxide absorbs the heat, the low temperature radiation from the Earth (heat) is prevented to leave into the atmosphere.

This is a serious problem, since this leads to heating of the atmosphere and also of the whole planet.

Since the Industrial Revolution, the world's average temperature has been raised by some ½ °C [6].

It is possible that the temperature will rise about another 1.5 to 4.5°C until the end of the next century if we do not change our energy consumption pattern, and replace the use of fossil fuels [20]. Wood, coal, gasoline and natural gas all have carbon dioxide as their main by-product of combustion.

What could be the consequences of the temperature increasing?[6]

- rising oceans
- killer hurricanes
- droughts
- floods

What is the human cost?[6]

- cardio-vascular problems, because of the heat
- heat-related deaths
- starvation due to drought or flood

D. Acidification

Criteria: *Minimising polluting gases which contribute to acidification, such as oxides of sulphur and nitrogen. At least, the polluting gases must not contribute to a further extension of the acidification.*

Indicators: NO_x , SO_2 [6]

The polluting gases sulphur dioxide and nitrous oxides contribute to sulphuric acid and nitric acid. These are very strong corrosive acids [6]. The concentrations of acid are increasing because of our large fossil fuel consumption.

Everything in our ecological system is affected through the acid rains, because of its corrosivity, which is very harmful to all living creatures. Acid rains occur when ordinary water vapour in clouds condenses into water droplets and mixes with polluting gases as they fall through the atmosphere.

Furthermore, the acid rains also damage forests and farms when acid precipitation soaks into the soil. The organic nutrient balance is disrupted when minerals and other compounds are dissolved. This results in illnesses and loss of calcium, leading to for instance cardiovascular diseases.

However, it is not only humans who are being exposed to these acid rains, but the aquatic life and all animals are also affected.

Acidification of lakes is a well known problem amongst most people these days. It has been reported that 14 000 lakes in Sweden alone have been acidified, and also that 4 000 of those are fish less [6]. Not only is the oxygen level being reduced, but hundreds of species of plants and animals are being extinct every year.

E. Toxic substances

Criteria: *Polluting substances which have a dangerous effect on the ecological system must be minimised. There should be no increase of cancer, smog or dirt caused by toxic polluting substances.*

Indicators: Peroxyacyl nitrate (PAN), benzopyrene, smog, CO and SO_2 [6]

There are a lot of gases, emitted from, for instance, combustion of fossil fuels, that are very dangerous to all life on Earth.

Smog is a phenomenon caused by exhaust gases from automobiles.

It is dangerous, because our bronchial tubes become irritated as we inhale smoggy air.

Nitrous oxide dissociates and forms nitric oxide and "active oxygen". When regular oxygen reacts with the "active oxygen", ozone, O_3 , is formed.

The ozone formed stays at ground level instead of forming the protective layer we need in the stratosphere.

This ozone, combined with carbon-containing compounds, produces PAN molecules.

Smog occurs when PAN condenses on pieces of fly ash or evaporate from a furnace fire, or on dust floating around in the air [6].

The human cost associated with these types of pollutants are irritation of the larynx, and also of the eyes (PAN). Even more serious is the fact that there is an increase of certain types of cancer related to gasoline or diesel (benzopyrene).

2.2.2 Summary of Indicators

Benzopyrene

Diesel fumes emits benzopyrene. It is the same chemical in cigarettes which causes lung cancer. It is not yet certain to what extent it may cause cancer when inhaled from diesel or gasoline fumes. Benzopyrene is the worst pollutant (of those mentioned in this text) as far as long term damage to the body is concerned.

Carbon dioxide

Carbon dioxide, CO_2 , is not a poisonous gas, but is harmful in other ways.

It is often called the "greenhouse gas", since it is one of the primary gases that contribute to the heating of the atmosphere and our planet.

Carbon dioxide occurs as a natural component in the atmosphere (it is for instance released into the atmosphere during volcanic eruptions), but the level is kept in balance most times, because of the carbon dioxide use in the photosynthesis process.

However, increasing the use of carbon containing fuels also leads to increasing the carbon dioxide level in the atmosphere to a limit where we get a large surplus of carbon dioxide [7].

Carbon monoxide

Carbon monoxide, CO , is colourless and odourless, and it is a poisonous gas produced while burning fossil fuels. However, the amount of carbon monoxide emission depends very much on the combustion conditions.

Human activities account for over half of the carbon monoxide in the atmosphere.

This gas causes perturbation of the stratospheric ozone layer, and also increased removal of hydroxyl radicals (OH) from the atmosphere [6][7].

This gas causes headaches, dizziness and confusion when inhaled. The red blood cells transport carbon monoxide to our heart and brains, instead of taking the oxygen there.

Chlorofluorocarbons, CFCs

CFCs are often used for air condition, refrigerators, freezers, etc. The effect of CFCs, as greenhouse gas, in the atmosphere is about ten thousand times higher per molecule, than the effect of CO_2 . CFCs can stay in the atmosphere for many thousand of years. Besides being a strong greenhouse gas, it does also effect the ozone layer in a negative way. The depletion of the ozone in the stratosphere has come to be a problem as important as the greenhouse effect [20].

Methane, CH₄

Emissions of methane can mostly be related to farming, garbage, industrial organic waste, waste from gardens, etc. It is a strong reactive greenhouse gas, which can stay in the atmosphere up to 10 years [20].

Nitrogen dioxide, N₂O

N₂O is emitted from different combustion processes, farming and fertilising of the land and rice plantations. This gas can stay in the atmosphere for about 100 years [20].

Oxides of nitrogen

Oxides of nitrogen, NO_x, is a common name for nitric oxide (NO) and nitrous oxides (NO₂).

While burning carbon containing fuels with air (which is a mixture of oxygen and nitrogen) we get some by products - carbon dioxide and water vapour.

But we also get another chemical reaction when the nitrogen in the air combines with the oxygen to form NO_x.

This substance turns into acid in our lungs when we inhale polluted air. The lungs lose capacity to absorb oxygen from the air (so less oxygen is passed into the blood stream), which leads to chronic shortness of breath and lung and bronchial illnesses such as emphysema, and might eventually result in death [6][7].

Oxides of nitrogen contribute to acid rain, which may effect terrestrial and aquatic ecosystems.

Peroxyacyl nitrate

PAN is short for Peroxyacyl nitrate, which is a substance occurring from burning of fossil fuels (gasoline).

It causes swelling and irritation of the larynx (the voicebox in the throat), and irritates the eyes. It makes it difficult to breathe, if inhaled sufficiently [6].

Sulphur dioxide

Sulphur dioxide, SO₂, is emitted from combustion of coal and oil. This is a strong corrosive gas. It is a colourless, very poisonous gas, with a sticky smell. The gas is not flammable, but solved in water, it is strong acid [7].

Tropospheric ozone, O₃

The ozone absorbs the infrared radiation from the ground, with the effect of higher temperatures in the lower atmosphere (troposphere). This type of ozone forms when sunlight reacts with oxides of nitrogen from for instance exhaust gases [20].

3. HYDROGEN

3.1 Background

In all animal- and plant tissue, hydrogen is an important component. In fact, about three quarters of the Universe's mass consists of hydrogen [8].

It might be interesting to know that the sun is almost 100 per cent pure hydrogen, like the planet Jupiter. Jupiter has a liquid surface and is then frozen followed by metallic hydrogen in the core [6].

At normal temperature, hydrogen does not smell and it is tasteless and colourless. It has got low viscosity, and also low value of evaporation enthalpy, along with rapid diffusion. Table 3.1 shows energy capacity per mass unit for hydrogen, compared to other materials.

hydrogen	33.5
natural gas	13.8
oil	12.0
coal	8.2
methanol	5.5
batteries	0.01

Table 3.1 *Energy capacity per unit mass for a few different fuels (kWh/kg) [8]*

The low density of hydrogen cause the energy content per unit volume to be lower than for any other fuel. However, the energy content per unit mass is the highest among all available fuels on the market.

Combustion of hydrogen is a very clean process where water (H_2O) is the main product when using oxygen as an oxidant.

While other fuels emits lots of different pollutants, hydrogen is free from most of those. The combustion results in oxides of nitrogen (NO_x), which can be reduced to negligible level through catalytic processes when using air [8].

Table 3.2 below shows what kind of pollutants different energy sources give rise to.

	CO	CO ₂	C _n H _n	SO ₂	NO ₂	Heavy metals
oil	X	X	X	X	X	X
natural gas	X	X			X	
solar energy						
hydrogen					X	

Table 3.2 *Different energy sources [9]*

It is possible to see that hydrogen is a very good alternative, compared to others, when only considering the pollutants above.

Among other applications through the years, hydrogen has been used for heating and lighting, in balloons and air ships (such as the "Hindenburg"), and as raw material in the chemical industry sector.

The annual utilisation world wide (1992) is about $5 \cdot 10^{11}$ m³ hydrogen, mainly for the production of ammonia and the processing of refinery products. About 99 % of the hydrogen is currently produced from fossil fuels [VII].

3.2 Solar Hydrogen

Hydrogen in itself is not a primary energy source, but an energy carrier. Therefore, hydrogen needs to be produced by using a primary energy source (like the sun, for instance).

This study only treats hydrogen production with the sun as a primary energy source - solar hydrogen. Production from fossil hydrocarbons will not be regarded since this is not a production method in relation to sustainable development.

The sun is an enormous potential energy resource considering the fact that solar irradiation is equal to 173 000 TW. Every year, the sun "produces" solar energy equivalent to 160 times the energy stored in proven reserves of fossil fuels in the world. This is more than 15 000 times annual use of fossil fuels, nuclear and hydro power world wide [5].

Of the solar irradiation, about 30 % is reflected immediately, 47 % is directly converted to heat in the air, earth and oceans, and about 23 %, is absorbed by water evaporation. Only a very small amount (less than 1 %) is used for the photosynthesis, and to drive winds and waves [5].

Bockris and Veziroglu describes very well, in their book [6, p75], what solar hydrogen is:

"Put simply, solar energy is converted to electricity; to get the electricity over long distances, or for use at night, the electricity is used to electrolyse water to produce hydrogen (only the electricity that is not needed immediately by business, factories and households is used in this process). The hydrogen is then sent through pipelines, just as natural gas is sent today, to cities and towns."

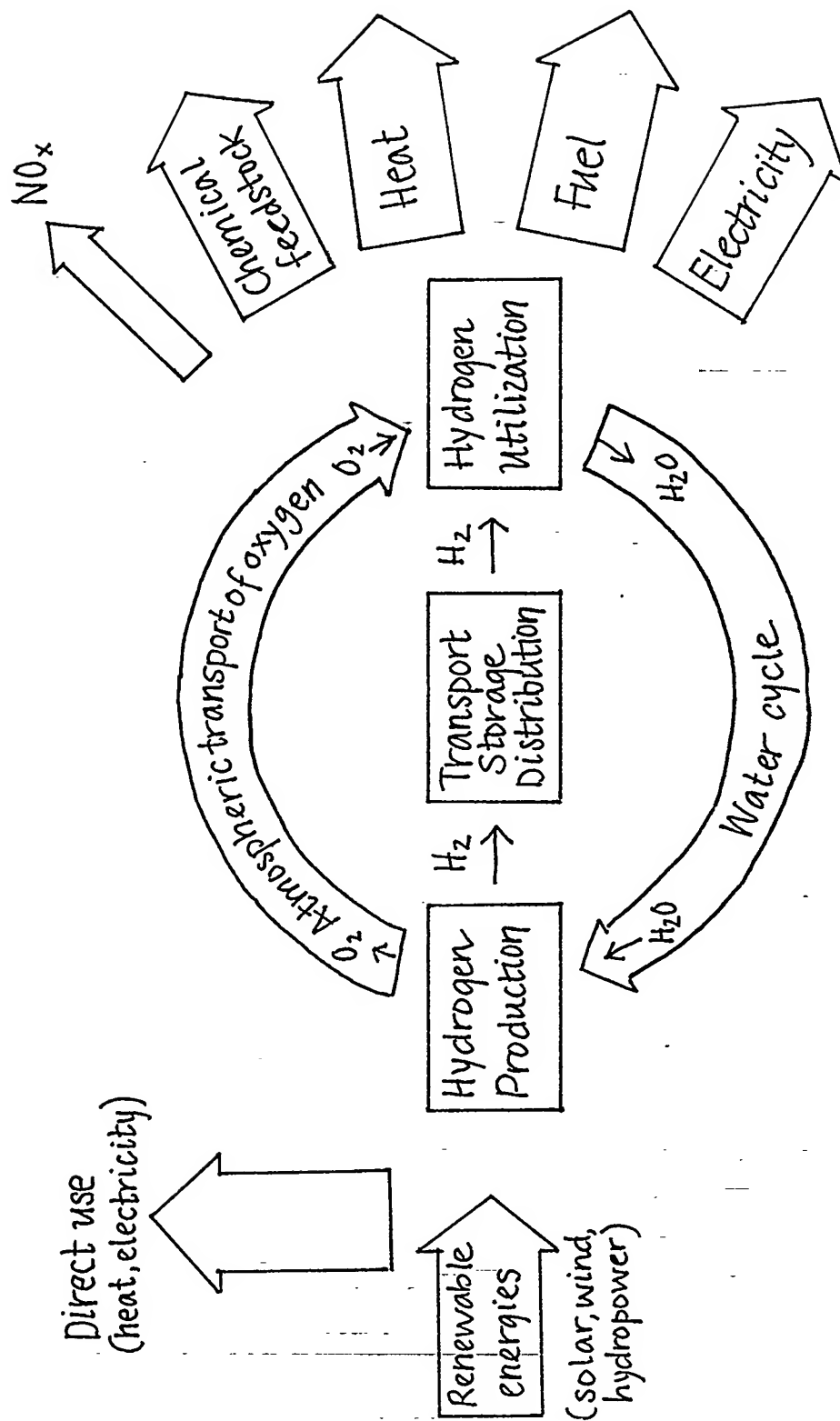


Figure 3.1. The hydrogen cycle based on renewable energy (solar, hydroelectricity, wind) [10]

What are the advantages, and disadvantages, compared to fossil fuels, with solar hydrogen?

	Fossil fuels	Solar hydrogen
Resources	Limited	unlimited
Effect on the environment	Dirty	clean
By-products	CO ₂ , NO _x , CO, SO ₂ , PAN	NO _x
Production cost	Cheap	expensive
Storage cost	Cheap	expensive
Transportation cost	Cheap	cheap

Table 3.3 *Fossil fuels compared to solar hydrogen*

3.3 Hydrogen Production

Hydrogen can be produced in many different ways with different primary energy resources.

Figure 3.2 shows different manufacturing types for hydrogen production, with different primary energy sources.

Steam reformation, partial oxidation and coal gasification are examples of hydrogen manufacturing with fossil fuels as the primary energy source. Today, steam reforming of fossil fuels is the most common, and economic, way to produce hydrogen. This method represents about 99 per cent of the hydrogen production. But since this production method contributes with a lot of CO₂, amongst other pollutants, to the atmosphere this is not a preferable method for the future, if we can not find a permanent way to store the CO₂.

In electrolysis, photon processes, thermolysis and thermochemical processes, renewable resources can be used as the primary energy source. The renewable resources, which for instance can be solar irradiation, hydropower, thermal or wind power, all have in common that they are not limited in time, but the quantity may be limited.

3.3.1 Electrolysis

Electrolysis is currently the most efficient method to produce hydrogen from water. In 1994, the share of electrolytic hydrogen on the market was less than 1 % [5].

There are three different methods for electrolysis

- A. Conventional Alkaline Electrolysis
- B. Solid Polymer Electrolysis
- C. High Temperature Electrolysis

These methods are all described further below in the text.

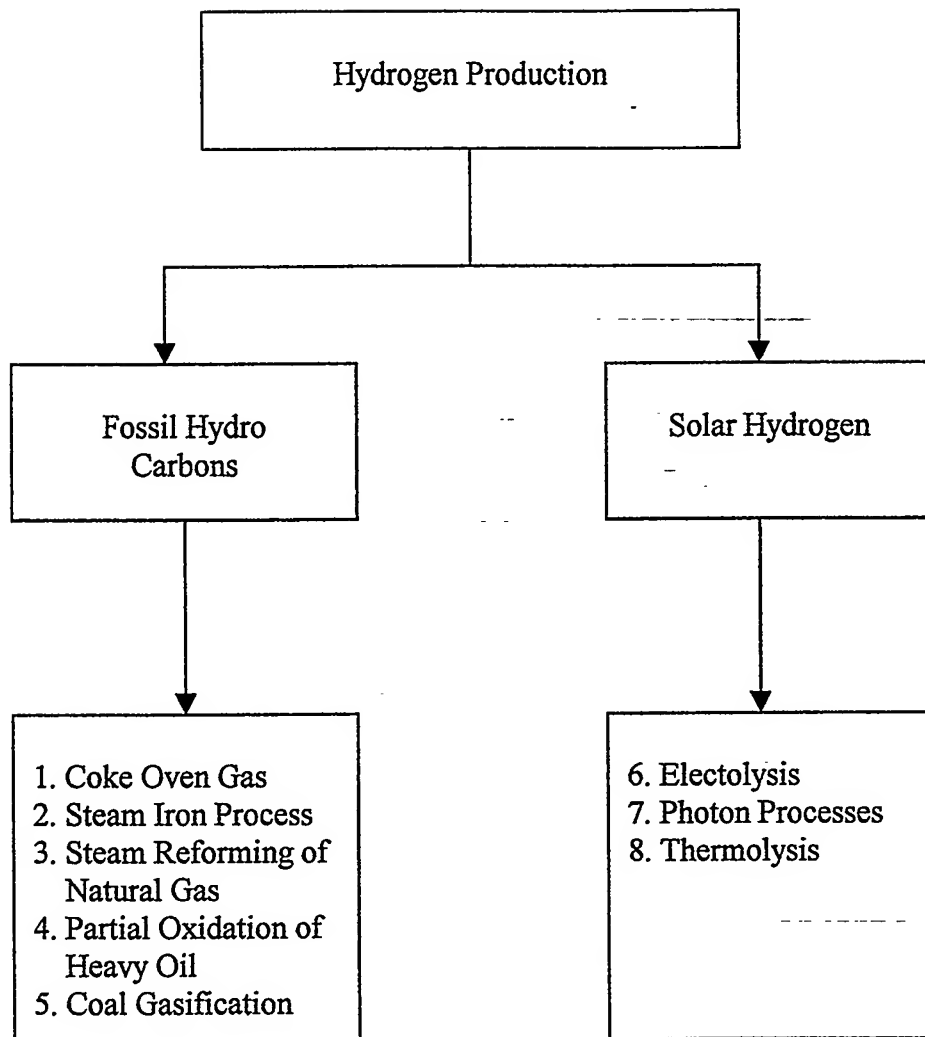
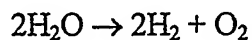


Figure 3.2 *Different ways to produce hydrogen*

A. Conventional alkaline electrolysis

The method of water electrolysis aims to split water into hydrogen and oxygen,



We can achieve this by lowering two electrodes into an electrolyte and then let a direct electric current pass through the electrolyte.

The electrochemical cell consists of two electrodes, an electrolyte and a diaphragm. In the commercial industry, the electrolyte is normally alkaline, and the diaphragm made of asbestos.

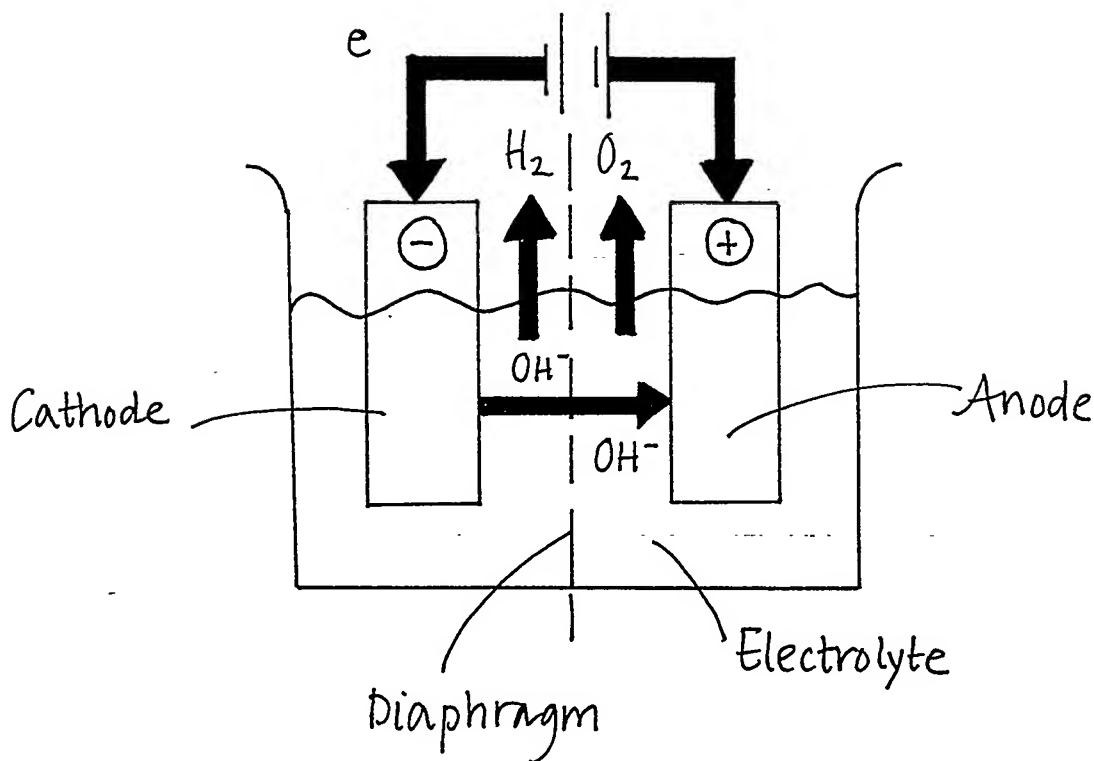
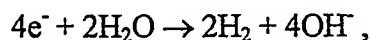
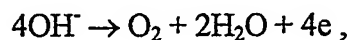


Figure 3.3 *Electrochemical cell for conventional alkaline electrolysis*

At the cathode we have



and at the anode



which means hydrogen is produced at the cathode, and oxygen at the anode. The diaphragm is necessary to keep these two products from remixing.

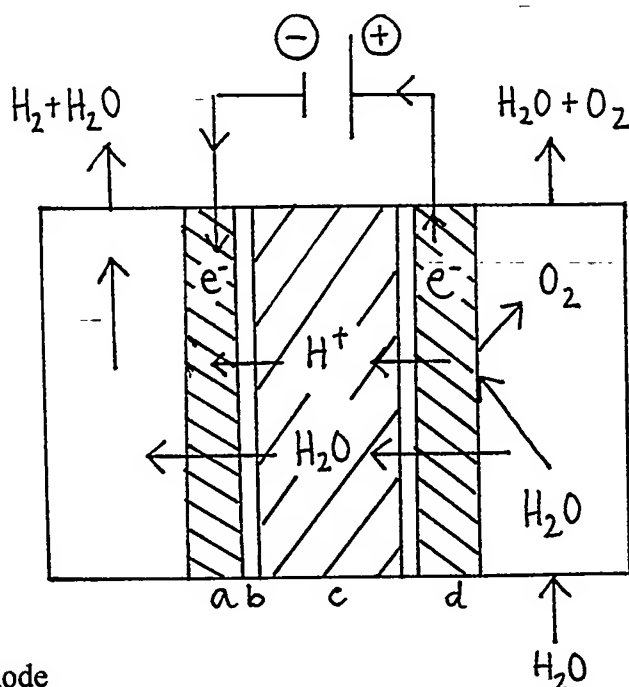
The amount of energy required for the process is measured by the cell potential, while the current density determines the hydrogen quantity produced per unit. The definition of the efficiency is hydrogen output divided by electricity input, hence both parameters are of interest for optimising the production.

Water electrolysis can be divided into two different groups according to their configuration, unipolar and bipolar. In the unipolar one, the electrolysis cells are connected in parallel, whilst the bipolar one have the cells linked in series. Most commercially available electrolyses have a bipolar configuration [8].

B. Solid Polymer Electrolysis, SPE

Besides the alkaline electrolysis we also have other methods for electrolyzers, of which Solid Polymer Electrolysis, SPE, is one.

In the SPE-method we have a proton conducting diaphragm which works as both electrolyte, in this method an acid one, and a diaphragm. The major advantage with this method is that it operates at high current density and low cell potential, which is good for optimising the production.



- a) porous cathode
- b) catalyst
- c) membrane, solid electrolyte
- d) porous anode

Figure 3.4 *Electrochemical cell for solid polymer electrolysis [11]*

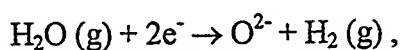
Due to the absence of the KOH electrolyte system, there is an extremely high volume reduction of the electrolysis unit. This way very high current density values can be achieved [11].

C. High Temperature Electrolysis, HTE

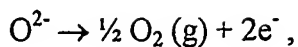
In the High Temperature Electrolysis, water vapour (800-1 000°C) flows through the diaphragm. The method requires a small amount of electricity, which is an advantage.

Series of cylindrical cell segments are used, where a thin layer of zirconium oxide (ZrO_2) work as diaphragm and electrolyte. The products (gases O_2 and H_2) is separated by putting the anode and cathode on different sides of the cylindrical cell segment, which leads to a transportation, through the diaphragm, of only the oxide ions, O^{2-} .

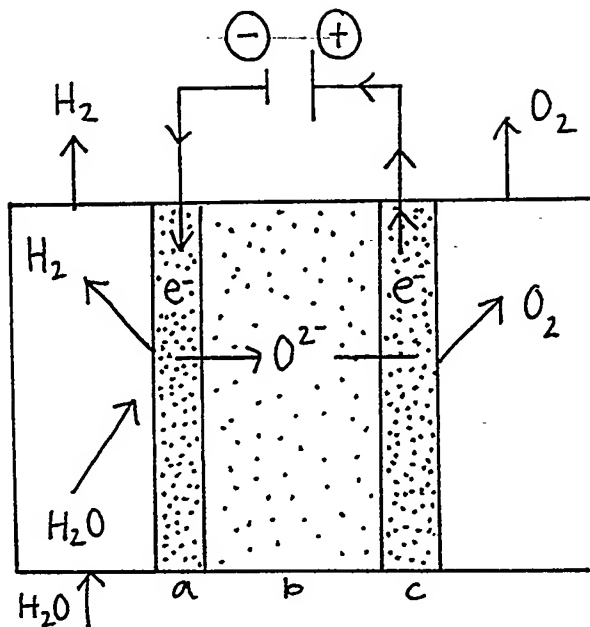
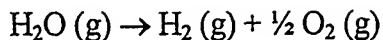
At the cathode we have



And at the anode



And for the cell



HTE cell using ZrO_2 solid electrolyte

- a) cathode
- b) electrolyte
- c) anode

Figure 3.5 *Electrochemical cell for high temperature electrolysis*

In table 3.4 energy demand and efficiencies are shown for the different methods of electrolysis.

Energy demand	Alkaline electrolysis	SPE	HTE	
			endotherm	exotherm
Electric energy (kWh/Nm^3)	4.30	4.20	2.60	3.20
Heat (kWh/Nm^3)	-	-	0.60	-
Water vapour (kWh/Nm^3)	-	-	0.60	0.60
η_{tot} (%) if $\phi=40\%$ for electricity	33	34	46	41
Conversion factor, H_2 (HHV) per kWh electricity	0.83	0.85	1.37	1.11

Table 3.4 *Energy demand and efficiency for production of 1 Nm^3 hydrogen*
 $\text{HHV}=3.55 \text{ kWh/Nm}^3$ [12]

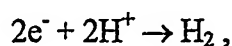
3.3.2 Photon Processes

There are mainly three different types of photoproduction of hydrogen

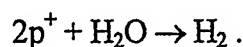
- A. Photoelectrochemical water cleavage
B. Photochemical production
C. Photobiological production

These are all direct production methods, which means that they produce hydrogen directly in solution using solar radiation, water and catalysts.

Water is split into gaseous hydrogen and oxygen using solar radiation. At the cathode we have



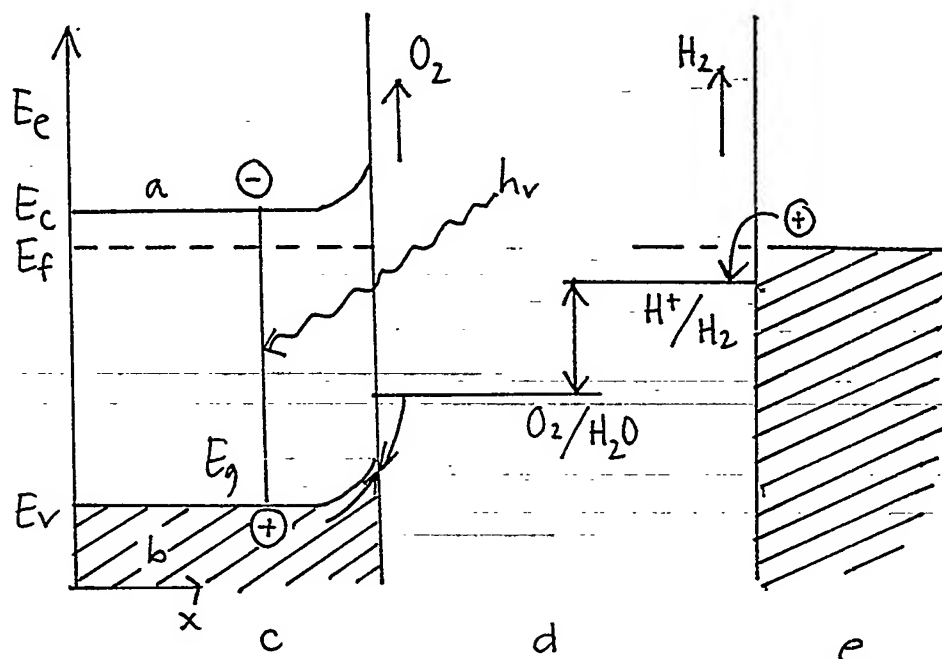
and at the anode



Photoelectrochemical water cleavage occurs if the water decomposition takes place on a macroscopic surface, photochemical in solutions on molecules and photobiological if the reaction takes place in a biological system [5].

A. Photoelectrochemical water cleavage

It is also possible to use semiconducting electrode materials (or semiconducting microheterogeneous particles) for cleavage of water.



- a) conduction band
b) valence band

- c) n-Type semi conductor
- d) electrolyte
- e) metal

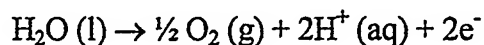
E_f : Fermi energy

E_g : Energy gap between valence and conduction band

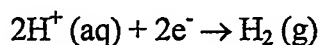
Figure 3.6 *Photoelectrolysis cell using n-type semiconductor anode (SrTiO_3) and a metallic cathode [11]*

The photoelectrochemical process is based on the band-gap absorption of photons by the semiconductor.

The electrons are elevated from the valence band to the conducting band creating electron-hole pair. Following this charge separation oxidation of water molecules at the surface of the n-type semiconducting anode takes place.



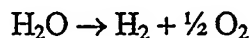
The cathode of the photoelectrochemical cell is made of a metal onto which hydrated protons are transported. Transfer of electrons from the Fermi level of the metal causes the reduction of hydrated protons producing molecular hydrogen.



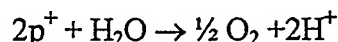
Experiments with single band-gap photoelectrochemical systems show an efficiency of about 10 % [5].

B. Photochemical production

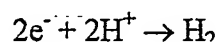
In a photochemical reaction, a sensitizer absorbs the sunlight and stimulates the process. The process that takes place can be described as a total reaction



At the anode, the oxidation takes place



and at the cathode we have the reduction



The sensitizer can be a molecule or a semiconductor.

Since this is a two-electron process, it is necessary to have a catalyst [5].

I have not found much literature about this process, and will therefore leave it at this.

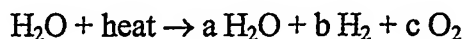
C. Photobiological production

Photosynthetic bacteria and microalgae can, for production of small amounts of hydrogen, through thermolysis, use solar energy as the energy source. For the absorption of light, some kind of chlorophyll is used. The photosynthetic bacteria also requires some organic carbon, for this complex process. Besides hydrogen and oxygen, carbon dioxide is also formed during the process. Efficiencies of about 10-12 % has been reported [5].

3.3.3 Thermolysis

The method of direct thermal cleavage of water is called thermolysis.

This process demands very high temperatures - about 2 700°C for 10 % dissociation of hydrogen at atmospheric pressure [11]. The water cleavage is possible since thermal and "free" energy is admitted.



Water can be divided thermally at temperatures greater than 1 700°C.

The thermolysis product of water is a mixture of different gases. The equilibrium composition depends on pressure and temperature of the reaction [8,11].

3.4 Hydrogen Storage

It is necessary to find ways to store hydrogen to be able to use it as a replacement for fossil fuels in motor vehicle applications. Since hydrogen has a very low energy density per unit volume, it demands lot of space while stored.

Hydrogen can be stored as gas, in liquid state or tied to other substances, like metal hydrides or hydrogen abundant chemical compounds.

Storage possibilities for hydrogen motor vehicles are

- liquid hydrogen in Dewar-containers or superinsulated tanks
- metal hydrides
- gaseous hydrogen in pressure tanks

3.4.1 Dewar Tanks

Liquid hydrogen storage requires less space, because we obtain a very high energy contents when converting hydrogen into liquid state.

Hydrogen is transferred to liquid state at -253°C .

Liquid hydrogen is advantageous to store since the density in this state is about 845 times higher than for gaseous hydrogen.

However, the technique is more complicated. The main reasons are the low value of evaporation enthalpy and the low boiling temperature of hydrogen.

These properties cause problems like

- choice of material for the equipment
- demands for better container insulation
- prevent leakage and temperature disruptions

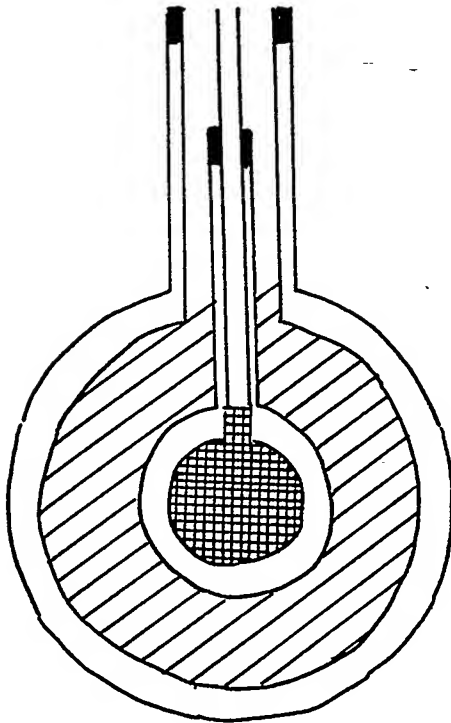


Figure 3.7 Principle for a Dewar tank [8]

About one third of the hydrogen's energy contents is consumed during the condensation.

The Dewar-tank is a vacuum insulated "bottle", invented by Dewar in 1898, for storage of liquid hydrogen. It consists of two concentric glass-tanks with room for insulation in between.

For small scale storage (less than 50 litres), it is possible to reduce the heat leakage by lowering the tank into an other Dewar-bottle containing liquid nitrogen. This corresponds to a reduced heat radiation factor of 230, and a temperature reduction of some 200°.

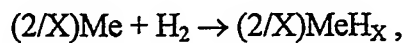
This method has very heavy tanks and needs a constant refuelling of nitrogen, which limits the volume.

Large tanks have a cylindrical shape with an inside wall, an insulation surface and an outside wall. This type of storage is, for safety- and construction reasons, suitable to place lowered into the ground.

The technique with Dewar-tank usage has been used in space-applications for a long time.

3.4.2 Metal Hydrides

Hydrogen is admitted into an other substance (metal or alloy), hydrogenation, while emitting heat. To disengage the hydrogen, dehydrogenation, heat is required. It is a reversible process.



where Me = metal or alloy, and
MeH_X = metal hydride

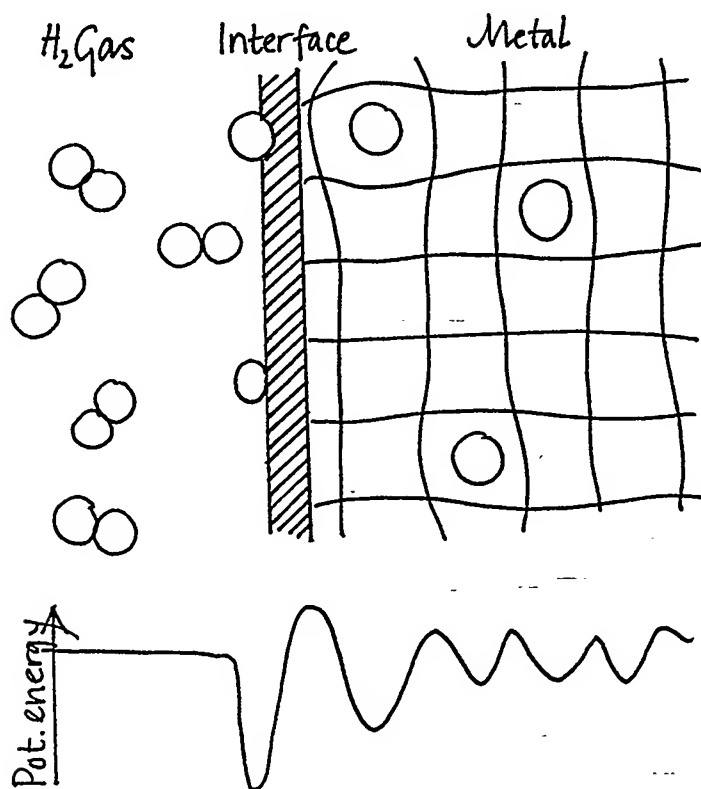


Figure 3.8 Mechanism of H₂ absorption in metals [11, p136]

Storage in metal hydrides permits good accessibility and gives a possibility for high storage capacity, because the chemically admitted hydrogen requires less space than liquid hydrogen.

Metals that might be considered suitable for metal hydride storage are, among others: magnesium (Mg) for temperatures above 473 K, titan (Ti), zirconium (Zr) or lanthanum (La), or different alloys.

For hydrogen storage in a large scale, Mg₂Ni or FeTi are preferable.

Magnesium alloys have a large capacity of hydrogen admittance, storage in pressurised tanks is not necessary, they react relative fast at acceptable temperatures, are air stable and comparative cheap.

Unfortunately, they are not free from disadvantages, because of the large required volume, large volume-expansion and high dehydrogenation temperature.

Important properties to consider when the choice of metal hydride is made

- character and strength of the chemical compound between hydrogen and metal/alloy
- swiftness while reacting
- temperature depending at equilibrium pressure

3.4.3 Gaseous Hydrogen Storage in Pressurised Tanks

Storage in gaseous state is attractive because both the production and end use of hydrogen often occurs in this state. This form of storage requires much space due to the low density of gaseous hydrogen. But if the gas is placed under pressure, less space is required. This is, however, a more expensive alternative.

There are two main types of gaseous hydrogen storage, namely underground storage and storage in pressurised tanks above ground.

Underground storage is seldom used and has not yet been well examined.

Merchant hydrogen is normally stored under pressure in a pressure cistern. This is a well known technique, and is mainly used for short-time storage.

3.5 End Use – Motor Vehicle Applications

Motor vehicle applications with hydrogen as a fuel is still on the experimental stage, and not yet on the commercial market for the public. So far hydrogen vehicles can not be cost-competitive with gasoline-powered vehicles. Hydrogen is more expensive to produce than fossil fuels. It is also necessary to use a different type of equipment for transmission, distribution, and fuel tanks, which will increase the cost even more.

But on the other hand, hydrogen can be produced in small-scale near the point of use. This can also minimise the distribution cost.

There are three major ways to use hydrogen to power vehicles [VIII].

- A. Conventional Internal Combustion Engine Vehicles (ICEVs)
- B. Fuel Cell Electric Vehicles (FCEVs)
- C. Hydrogen Hybrid-Electric Vehicles (HEVs)

ICEVs

It is possible to use hydrogen in an internal combustion engine, originally designed for gasoline. However, most experimental hydrogen vehicles have been equipped with modified internal combustion engines [IX].

Hydrogen has the highest efficiencies, lowest operating temperatures, and lowest emissions in internal combustion engines of any fuel [VIII]. It has been shown that hydrogen powered ICEVs are from 15 to 100 per cent more energy efficient than comparable gasoline powered vehicles. This is due to the low fuel to air ratio which can be used in hydrogen engines [IX].

The only pollutants produced from hydrogen ICEVs are NO_x . While using, for instance, water injection, lean operation, and exhaust-gas recirculation the NO_x emissions can be kept at very low levels [IX].

One major obstacle for the use of hydrogen ICEVs on the market today, is the problem of fuel storage onboard the vehicle.

Liquid hydrogen is not easy to store at ambient temperature and pressure. Onboard storage systems for hydrogen are much heavier and bulkier than those for gasoline or methanol.

A multi-layer insulation cryogenic tank would take up at least 49 litres of hydrogen, yielding a 189-liter fuel tank [VIII]. It is also necessary to use much hydrogen to reach adequate range. Calculations show that it requires about 30 litres of liquid hydrogen to travel 100 km.

If hydrogen was to be stored as compressed gas, it would take more than twice as much space.

Neither is it favourable to store hydrogen in metals, because of the weight (130 kg) and the auxiliary equipment required.

FCEVs

In this option, a fuel cell, powered by hydrogen and atmospheric oxygen, is used to generate electric power onboard at very high efficiency. The NO_x emissions will be eliminated, and the efficiency would be as much as possibly three times that of gasoline ICEVs [IX].

It is possible to store the hydrogen fuel directly onboard as compressed hydrogen gas, or in a hydride, or in the form of methanol (which is reformed onboard to produce hydrogen).

Unfortunately, the production cost of this type of vehicles is very high, due to the high cost of the fuel cells. Since each fuel cell does not generate more than 0.8-0.9 V, it is necessary to connect several cells in a series to obtain required voltage, which increases the cost considerably.

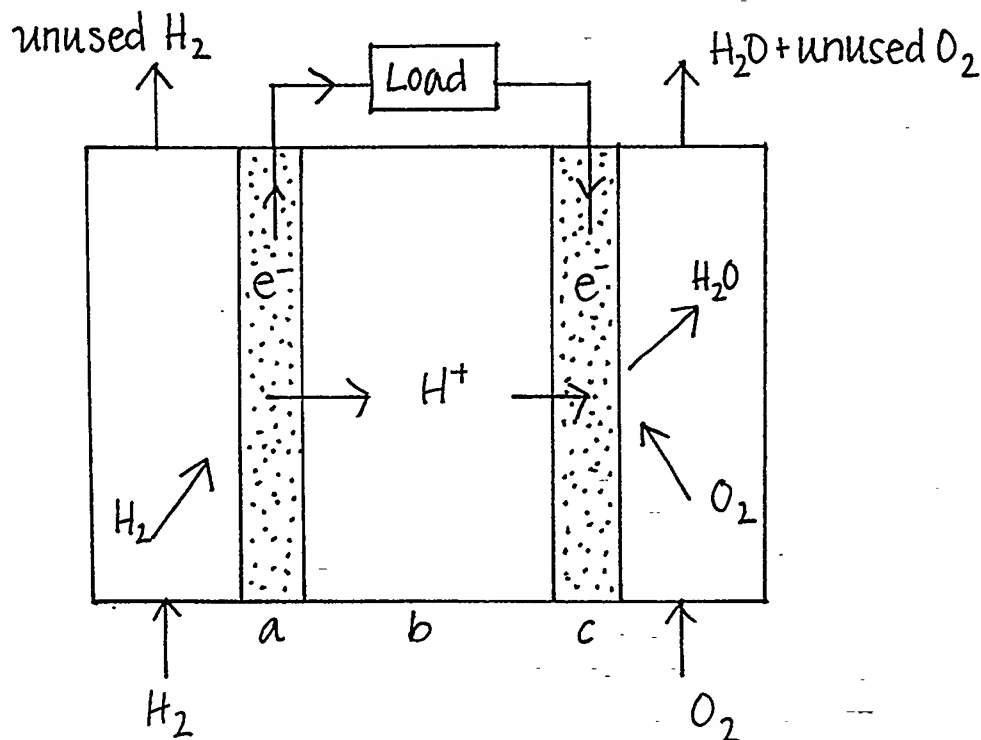
Among the various types of fuel cells which have been considered for transportation applications, the proton-exchange-membrane (PEM) fuel cell is most attractive. The PEM fuel cell offers high power density, quick start-up and modest operating temperatures (about 100°C).

The FEVER-project

The FEVER-project is a co-operation between Renault, Ecole des Mines de Paris, Ansaldo, Air Liquid, Volvo and de Nora S.p.A, partly financed by the European Commission. They have been working closely together for three years with the development of a fuel cell powered passenger car [XI].

The car has an electric motor, which is powered by a module consisting of the solid polymer fuel cells, their ancillaries and the liquid hydrogen tank. At start-up, the ancillaries are powered by a buffer battery, which also supplies complementary energy to the electric motor [XI].

In this project the fuel cells used are solid polymer fuel cells (SPFC).



- a) anode (H₂ electrode)
- b) ion exchange membrane or solid electrolyte
- c) cathode (O₂ electrode)

Figure 3.9 Principle of a solid polymer fuel cell [11]

SPFC systems have considerable commercial potential for transport applications as replacement for internal combustion engines. It's operating temperature is about 70°C, and it works with sulphated polytetrafluoroethylene as electrolyte.

There are many advantages with using this type of fuel cells in the project. For instance, with the SPFC high efficiency can be reached, along with low operating temperatures and fast start-up. It has no moving parts, low noise and absence of corrosive liquid electrolyte.

In this project, three stacks are connected in series. Their total weight is 320 kg, and their volume 225 dm³ [XI].

In table 3.5 the important data for the FEVER-car is shown.

Range	500 km
Top speed	120 km/h
Rated power	30 kW
Weight	2 200 kg
Liquid hydrogen onboard	8 kg
Air compression	3 bar absolute
Fuel cell	3 stacks of 10 kW each
Emissions	pure water

Table 3.5 *Technical characteristics of the FEVER-car [XI]*

HEVs

In the third option, an ICE is combined with electric motors, which makes it possible to achieve nearly the efficiency of a fuel cell, but at much lower cost.

Many different versions of HEVs are under development. Below follows a description of one of the prototypes built in Germany.

The design is a hydrogen powered vehicle with an electric drive-train. The fuel can be stored as compressed hydrogen or as liquid hydrogen or as lightweight hydride. Calculations shows that about 11 litres liquid hydrogen is necessary for a 100 km range. The hydrogen is used in a small optimised ICE (40 kW), or a PEM fuel cell, to run a generator charging an electrical storage system that in turn will power an electric motor to drive the wheels. The weight of the car is 1 140 kg (empty). Emissions from this vehicle will only be water and small amounts of NO_x [VIII].

4. METHANOL

4.1 Background

Alcohols (methanol and ethanol) have been used as motor vehicle fuels for a very long time, but not permanent and commercially as gasoline. They are especially suitable for use in Otto-motors.

Of later years it has been of interest to use alcohols (methanol, CH_3OH , and ethanol, $\text{C}_2\text{H}_5\text{OH}$) as fuel for motor vehicles. One reason for this, among others, is the environmental aspect. It is of interest to reduce the emissions from for instance compression ignition engines to reduce the greenhouse effect.

If we compare alcohols with gasoline, there are many advantages for the use of alcohols [14, 15, 16]

- lower NO_x and HC emissions
- ozone formation in the lower air layers is reduced thanks to differences in exhaust composition (e.g. HC spectrum)
- lower evaporation rate
- emissions of CO_2 are limited by using alcohols instead of gasoline or diesel fuel
- no sulphur contents
- the only health hazard occurs if the substance is consumed (eaten), e.g. no cancerogene qualities

Combustion of methanol leads to exhaust gases such as aldehydes and formaldehyde, and also unburned alcohols.

Unfortunately, methanol has a low energy content, responding only to about 50 % of the value of gasoline. However, methanol is easy to handle, while it is liquid and can be treated pretty much as gasoline. It is also less flighty, resulting in less evaporation loss in the distribution and end-use chain. Risks for fire and explosion are less for wastage in the open air, but potentially higher for storage in closed tanks (compared to gasoline) [16].

4.2 Raw Material

Methanol can be produced from many different sources, like natural gas, naphtha, oil, coal, peat or biomass [16].

Today, most methanol is produced from natural gas. Oil and coal used to be the raw material, but now, natural gas is a better alternative. While using natural gas as the primary energy source, an efficiency of 65 % can be reached for the methanol synthesis. If biomass is used, the efficiency will only be about 45 % [21].

Natural gas, naphtha, oil and coal are all in the category of fossil fuel, and do therefore not fulfil the demands for sustainable development. There are different opinions when it comes to peat, weather it is a fossil fuel or not. I will consider it as a renewable resource in this report.

Bioenergy is a common name for all sorts of animal- and plant tissue used for energy purpose. The biomass can be converted into different kinds of refined energy carriers like wood chips, biogas, wood powder etc [1].

Figure 4.1 shows different raw material groups, and what they can be used for. Cellulose rich plants are suited to produce ethanol and methanol for use as fuel in motor vehicles.

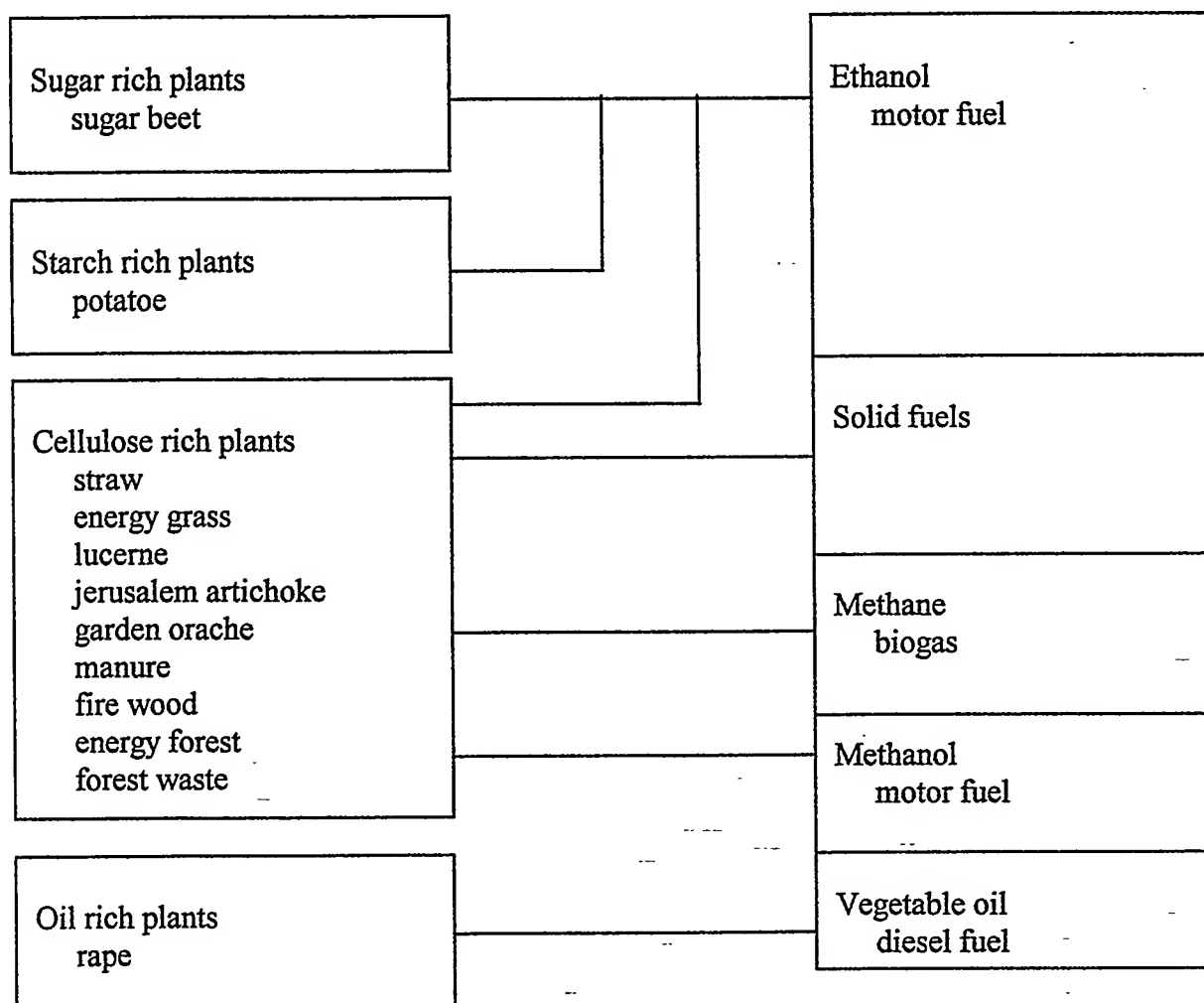


Figure 4.1 *Example for use of energy wood and energy crops [1]*

There are many advantages with using biomass in the energy system

- biomass is a renewable resource
- biomass is more accessible than fossil fuels in Sweden
- the consumers are interested in modern and cleaner energy carriers
- biomass can be produced at competitive prices in the future

Motor fuel can be the final product from the biomass. The common name is biofuel. It can be produced either from wood or from agricultural crops. Figure 4.2 shows the different biofuel categories.

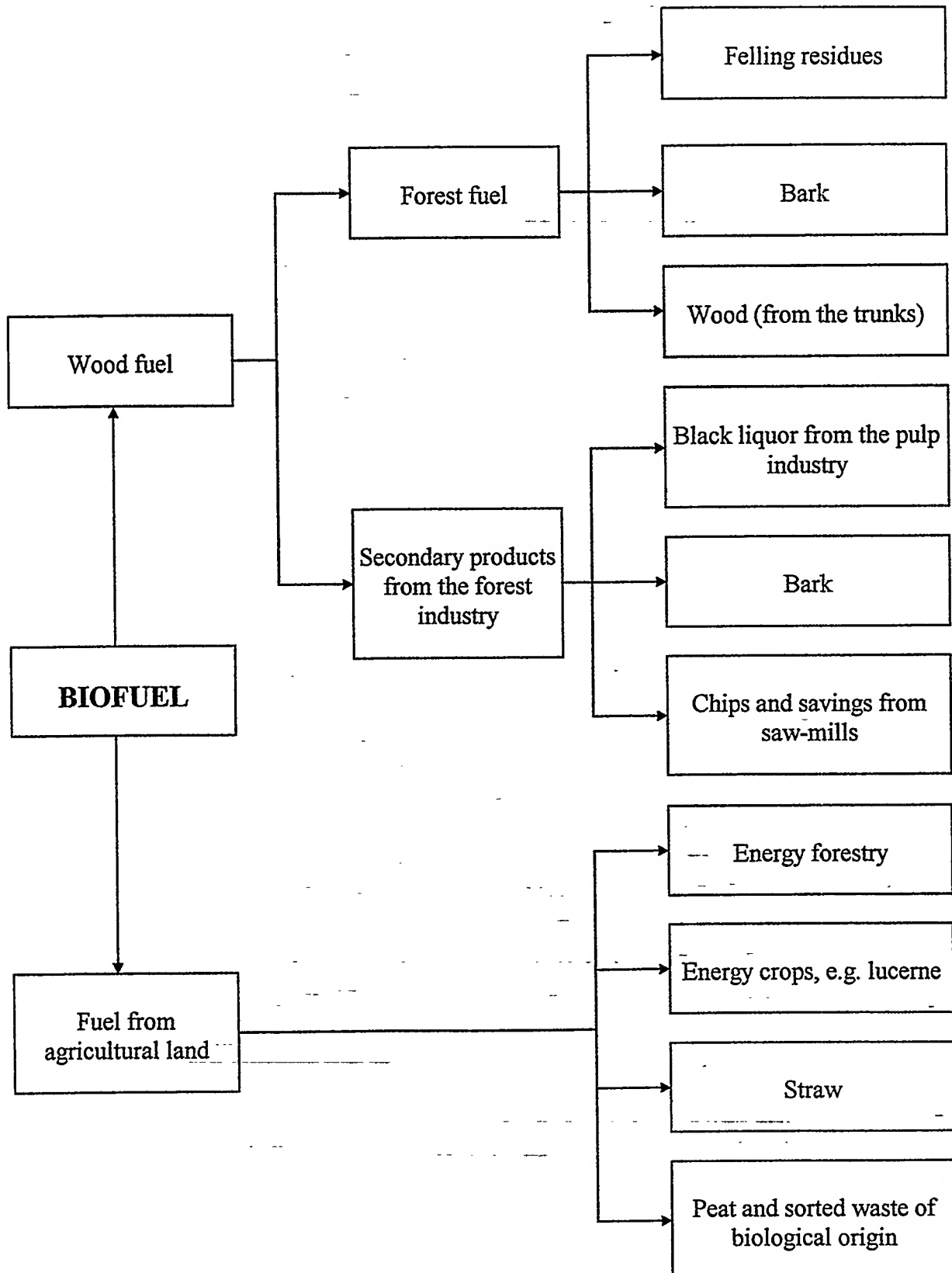


Figure 4.2 Biofuel categories [17]

Possible existing domestic raw material for producing methanol sustainable are

- peat
- fuels from wood
- energy forests
- straw

Peat

Peat is a finite supply of raw material, while it takes about 1 500 years to form a one meter layer.

In Sweden, the growth of peat is equal to about 10-12 TWh per year. The total surface is about 6 mil hectares of which 350 000 are extractable. In 1991, the Swedish production of peat for energy purpose came to 2.6 millions m³, which equals to 2.4 TWh [18].

Energy plantations

Another domestic possibility is to produce methanol based on usage of energy plantations for syngas.

The research and development of these production methods began in the middle of the 1970:ies, with the aim to enable a reduction of the import of fossil fuels.

There is a large potential for growing energy plantations on fields not used for grains or other agriculture products.

Energy plantations normally consist of fast growing willow or sallow, and it needs to grow where there is easy access to water.

It is possible to harvest every 3-5 years up to 5-6 times. After every harvest it grows new crops.

The energy content of this product is about 16 000-18 000 kJ/kg dry substance, and it is possible to receive about 12 000 kg dry substance/year and hectare [18].

Storage of wood fuels

The moisture content, which is the quotient of the weight of the water in a damp material and the total weight of the material, is of large importance while calculating the heating value. At 50 % moisture content, we get a heating value of about 17.1 MJ/kg DS (dry substance wood rests), but if we lower the moisture content to 40 %, we get a 5 % increase of the heating value, to 17.9 MJ/kg DS.

It is possible, with a start value of the moisture content of 55 %, to achieve a moisture content of 20 %, if we store wood chips stacks under roof for seven months.

The equal content for storage outdoor, without roof, is 50 % [16].

Loss in substance value occurs both in form of loss of wood rests and material, while handling the raw material, as well as through chemical subversion caused by micro organisms and chemical oxidation processes.

It is preferable to store the raw material in small well ventilated wood chips stacks, both to reduce the substance loss, but also to get a low moisture content. All to all, the highest heating value is obtained through storing the wood fuel where the moisture content is being reduced, and the substance losses minimised.

4.3 Production of Methanol

The production is a two step process where a synthetic gas (syngas) first is produced and then converted into methanol. The syngas can be produced from for instance natural gas, naphtha, surplus oils, lignite, peat or biomass.

Today's production is mainly based on the use of natural gas.

From an environmental point of view, it is preferable to use biomass for the syngas production, since the net discharge of carbon dioxide is eliminated.

Biomass conversion

Most types of biomass can not be used directly as fuel, but need some kind of conversion before usage.

Compared to fossil fuels, fresh biomass has a very low thermal content.

The moisture content is very high, resulting in a significant energy loss during combustion. Further on, large equipment for handling, storage and combustion are acquired because the low bulk density of biomass.

An other problem with fresh biomass, is the physical form, since it is often not homogenous and free flowing. This causes difficulties, considering pumping or vehicular transportation metering, storage and feeding to end use equipment.

The goal with the biomass conversion is to improve the characteristics of the raw material so we can use it in an energy system.

During the conversion, the water content of the material, is reduced, why the thermal value increases.

The conversion also includes an improvement of the handling characteristics of the material (solid material into fluid, i.e. gas or liquid).

Biomass can be converted either thermally or biologically [19].

The main thermal conversion processes are

- Carbonisation - charcoal production
- Pyrolysis - pyrolytic oils production
- Gasification - producer gas production

The biological conversion processes are

- Anaerobic digestion - biogas production
- Hydrolysis - ethanol and methanol production

4.3.1 Methanol from Biomass

While using biomass as raw material for methanol production, the raw material is gasified with oxygen and vapour, and then further refined and cleaned to a syngas.

A flow scheme for methanol production from biomass may look as figure 4.3.

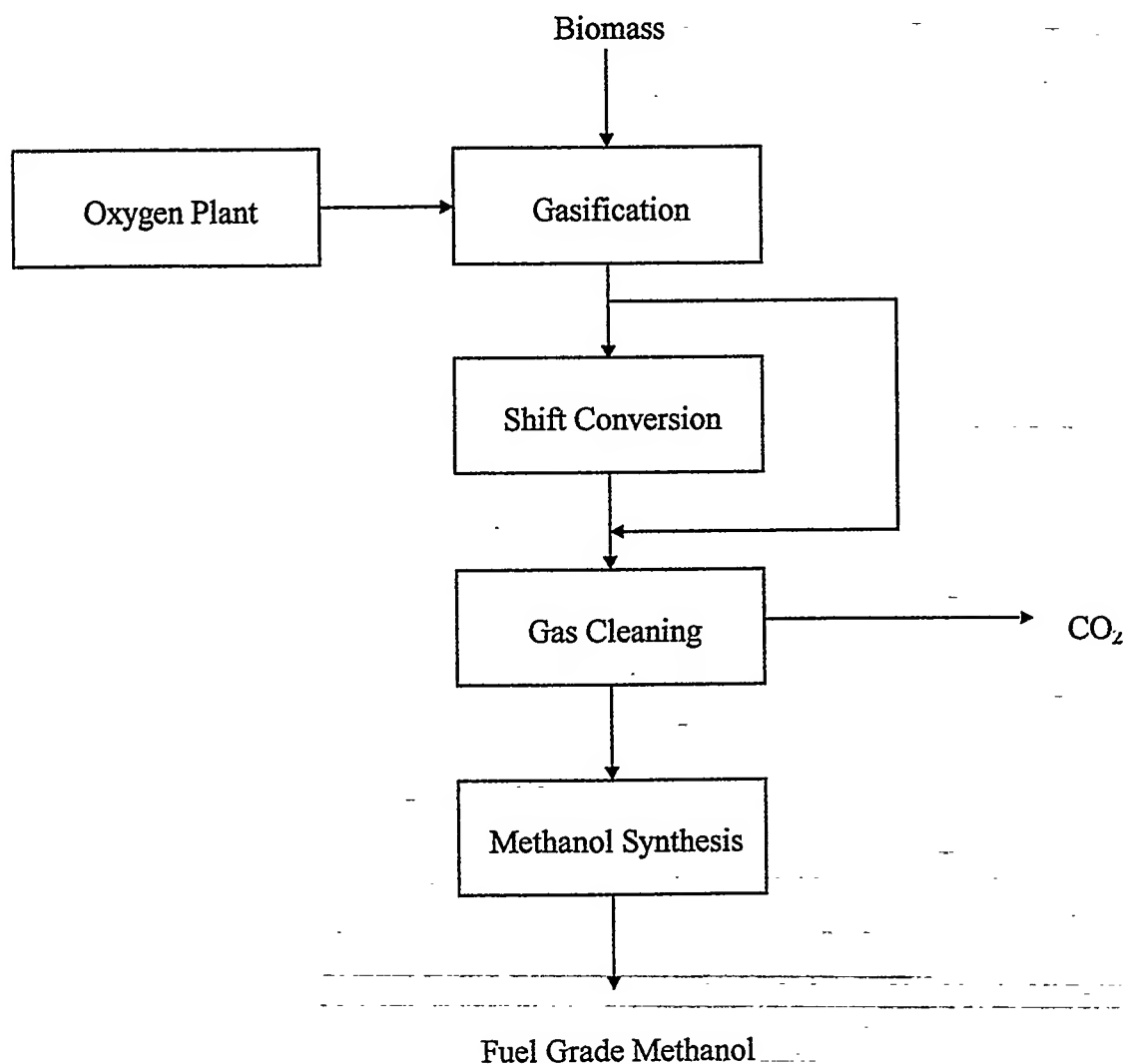


Figure 4.3 *Production of methanol from biomass - flow scheme [16]*

A catalyst is used to adjust the hydrogen/carbon monoxide ratio by letting some carbon monoxide react, with water vapour and carbon dioxide, through the catalyst. The gas is then cooled and cleaned, by absorption, from hydro sulphide and carbon dioxide, after which sulphur and carbon dioxide are extracted from the solvent.

A. HTW - High Temperature Winkler

The High Temperature Winkler-process, HTW, is developed by Rheinbraun, Germany, for the use of brown coal as raw material.

A flow scheme for the process is shown in figure 4.4 below.

The fuel is added in to the reactor, in which the gasification takes place in a fluidised bed. Steam and oxygen are the reactants in this process which takes place at 910°C and 1.1 MPa. More oxygen, secondary oxygen, is added to remove the tar from the reaction.

In the cyclone, the fines are separated, and the gas is then cooled and scrubbed. The cooling is performed through direct contact with water. The gas only admits the amount of water needed for the carbon monoxide-conversion.

All unnecessary sludge is discarded, and the hydrogen/carbon dioxide ratio is adjusted with the help of the carbon monoxide-conversion before the compression.

CO ₂ removal	7-8 %
Cooling	19-24 %
Oxygen	4 %
Drying	13 %
Grinding of the fuel	4-6 %
Fumes	4-5 %
<i>Total</i>	<i>45-60 %</i>

Table 4.1 *Energy losses for the HTW-process based on the use of wood fuel, moisture 50 % [15]*

B. MINO - Minimal Oxygen Process

The MINO-process has been developed in Sweden for production of methanol with minimal oxygen use.

The input in the process, the dried fuel, often consists of peat, wood or lignite.

The process is shown in figure 4.5 below.

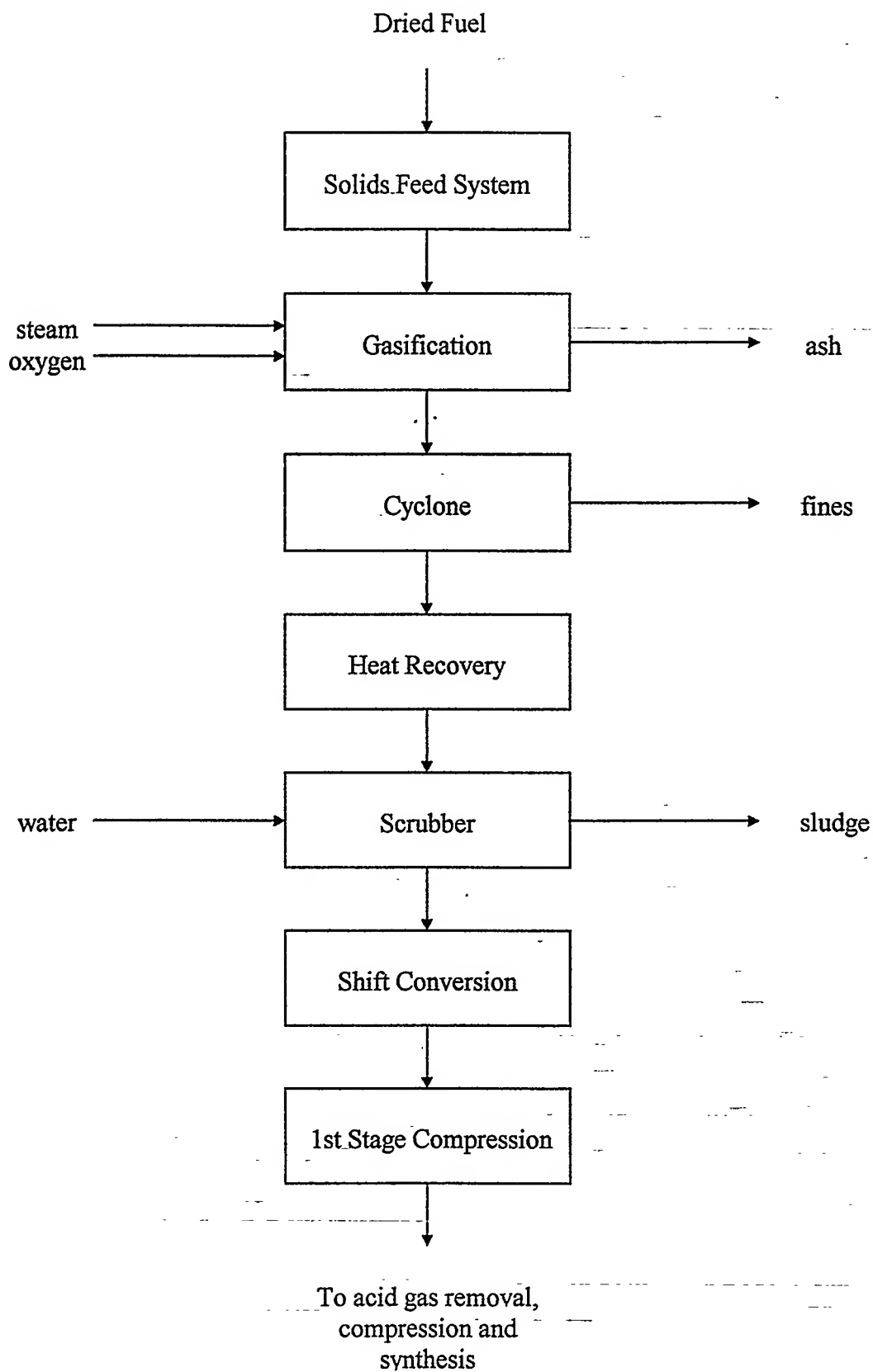


Figure 4.4 Flow scheme for the HTW-process [15]

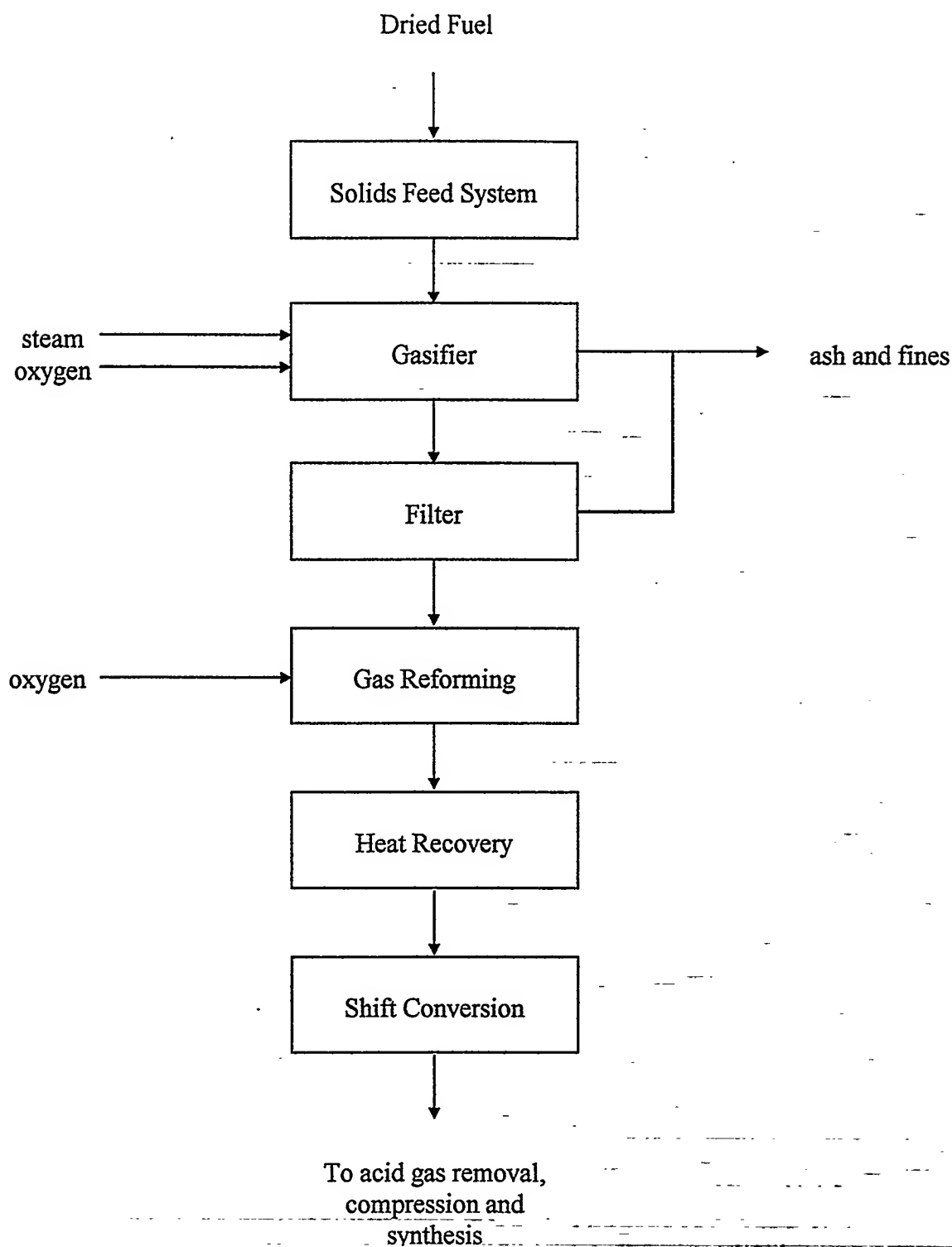


Figure 4.5 Flow scheme for the MINO-process [15]

The dried fuel is supplied to the process via a system where it is pressurised with gas to 10-30 bar, and then submitted into the primary gasifier, which has a working temperature of 700-800°C. There, the fuel is pyrolised through contact with a fluidised bed, which is kept floating by steam adding.

To keep the temperature at a desirable level, oxygen is added.

Ashes and fines are separated at the bottom via a cooling screw, and discarded.

Raw gas with an abundant content of methane, but also containing tar (gas state) and dust, is the product from the fluidised bed.

The dust is mainly separated in a cyclone for recirculation to the bottom of the gasifier, making the coal transformation increase.

The gas is filtrated through a high temperature filter to remove the rest of the ashes and fines, and then treated in a secondary stage.

The purpose of this secondary stage is to improve the gas quality by using a catalytic solid bed working at 900-1 000°C (it is possible to use a solid bed, due to the high degree of dust separation).

The oxygen use is diminished because of the catalyst's effect to destruct the tar and methane at relative low temperatures.

The end-product is a dust- and tarless gas with low content of methane.

Advantages with this concept [15]

- higher degree of efficiency compared to the HTW process
- low oxygen consumption
- improved heat recovery from the dust- and tarless gas
- no heat loss, since there is no need for a scrubber
- less expensive thanks to the simplicity

4.4 Methanol as Motor Vehicle Fuel

Alcohols (methanol and ethanol) are considered to be highly refined fuels with good combustion qualities in engines, gas turbines and furnaces, together with the fact that they are easy to store and distribute.

Alcohols consist of very simple molecules containing only coal, hydrogen and oxygen. There is no form of pollution of sulphur or chlorine, because of the good refining which makes it possible to fulfil strict environmental demands. These factors together make methanol and ethanol suitable candidates to gasoline as fuel for motor vehicles.

Calculations show that while extracting raw oil for gasoline/diesel production, about 12 % of the energy content in the raw material, is being used for the extraction, transports, refining and distribution (9.5 % for refining, 1 % for extraction, 0.6 % for transportation to refinery and 0.9 % for distribution to end user) [16]. The responding figure for methanol use in Otto-engines are about 10 % lower than the one for gasoline, and about the same as diesel oil for methanol use in a diesel engine.

Distribution of substances that are dangerous for our health and environment are much lower for biomass as raw material, than alcohols based on gasoline from raw oil or diesel oil.

The low sulphur content in the biomass contributes to a very low level of acid gas emissions. An other advantage with methanol produced from biomass, is the lack of aromatic compounds (benzene, etc.) and PAC, as well as the low emissions of alkenes and formation of reactive oxidant substances.

Emissions of aldehydes are higher, as could be those for alkyl nitrites.

However, all to all, alcohols are to prefer rather than disregard.

4.4.1 Methanol Fuel Cell Vehicle

New on the market is Necar 3. This is a passenger car from Mercedes, driven by fuel cells [X].

The fuel chosen for the car is methanol, and not hydrogen. This is to avoid problems connected with hydrogen - such as storage, distribution and refuelling.

The car has a chemical reactor in the back, where hydrogen is extracted from methanol. Water and methanol are evaporated at about 280°C, where water, carbon dioxide and carbon monoxide are formed. The carbon monoxide reacts, in a catalyst, with the oxide in the air to form carbon dioxide [X].

The fuel cells used in Necar 3 are proton exchange membrane fuel cells (PEMFC). They are well suited for mobile applications, because of their operating temperatures of 20-200°C and their high power density.

The PEM fuel cell has two electrodes, separated by a polymer electrolyte. Each of the electrodes is coated on one side with a platinum catalyst. At the anode, hydrogen fuel is dissociated into free electrons and protons. The electrons are conducted in the form of useable electric current through the external circuit. The protons migrate through the membrane electrolyte to the cathode. There, they are combined with oxygen from the air and electrons from the external circuit to form pure water and heat [11].

The fuel cells used in Necar 3 are produced by Ballard, in Canada. The cost for the fuel cells is still very high, about 25 000 SKr/kW. In order to produce the car for the public, the cost needs to be reduced with at least 90 %.

The degree of efficiency for this kind of car is very high, theoretically about 60 %. In the project with Necar 3, 40 % has been reached. With Necar 3 and a 40 litres tank, the range is about 400 km[X].

Since this Necar 3 does not need hydrogen tanks and batteries, the weight of the car is reduced. The everyday practicality of the car is improved, because it is possible for filling stations to handle methanol without any special safety measures. If there will not be a distribution net for methanol, it is possible to produce versions of the car where gasoline or diesel oil are converted to hydrogen. However, this is a more complicated procedure, which will affect the degree of efficiency negatively.

5. CHARACTERISATION

5.1 Characterisation Method

In the presentation of the characterisation, I will use a kind of star diagram, where it is possible to see what kind of emissions we get from different fuels. From the diagram is easy to see whether the criteria are fulfilled or not, and to what degree.

To have something to compare the diagrams with, I will first present two diagrams in figures 5.1 and 5.2. Figure 5.1 shows the different indicators while using a zero emission vehicle (ZEV). An electric car can be considered to be a ZEV. Only the circle in the middle is filled, since we have no pollutants.

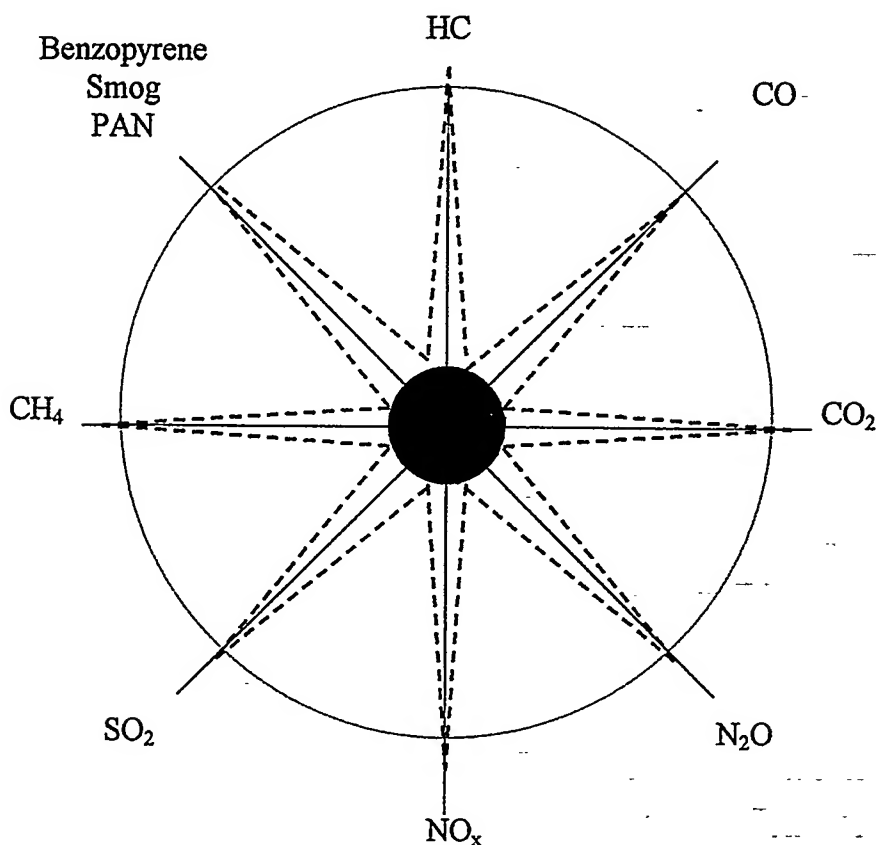


Figure 5.1 Zero emission vehicle

In figure 5.2, the same diagram is shown for an ordinary motor vehicle driven with gasoline.

Ordinary motor vehicles have different emission values depending on whether it is a new vehicle or an old vehicle, or if it has a three-way catalytic exhaust device or not.

Table 2.1 shows the exhaust values for a passenger car with a perfect catalytic exhaust device from 1990.

	New passenger car with catalytic exhaust device
NO_x	0.20
HC	0.13
CO	0.94

Table 5.1 *Exhaust values (g/km) for a new passenger car with perfect catalytic exhaust device [21]*

Table 5.2 shows the same emissions from a passenger car, with a catalytic exhaust device, which has been driven for about 5 years.

	Passenger car with catalytic exhaust device 5 years later
NO_x	0.47
HC	1.30
CO	2.30

Table 5.2 *Exhaust values (g/km) for a passenger car, with catalytic exhaust device, after 5 years in traffic [21]*

The result is, as can be seen, that the catalytic exhaust device will have reduced effect after a few years. However, it is still much better than the option to drive a car without a catalytic exhaust device. Table 5.3 shows the emissions for a car, without catalytic exhaust device, from the late 1970s.

	Passenger car, without catalytic exhaust device, from the late 1970s
NO_x	1.80
HC	1.90
CO	18.0
Particles	0.50

Table 5.3 *Exhaust values (g/km) for a passenger car, without catalytic exhaust device, from the late 1970s [21]*

Today, the pollutants of an ordinary, average passenger car are many. In this report HC, CO, CO₂, N₂O, NO_x, SO₂, PAN, Benzopyrene and smog are mentioned and registered on the axis in the diagram.

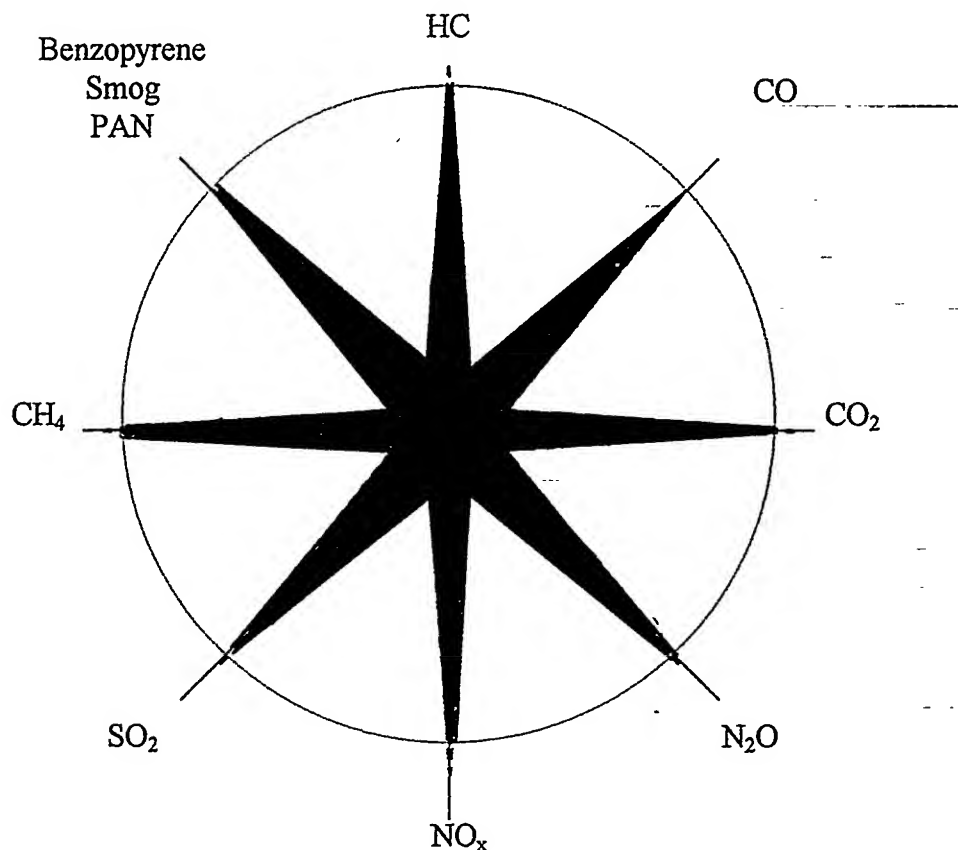


Figure 5.2 *Emissions while using gasoline as motor vehicle fuel*

Here, we can observe that the whole star is filled, because of all emissions from this type of fuel. However, the scale of the axes are not in proportion to each other. This diagram is only to show the different types of pollutants, and if they exist or not.

5.2 Characterisation of Hydrogen

If hydrogen is produced from a renewable primary resource, combustion of hydrogen is a very clean process. The main product received is water, and the only type of pollutants we have to consider is NO_x.

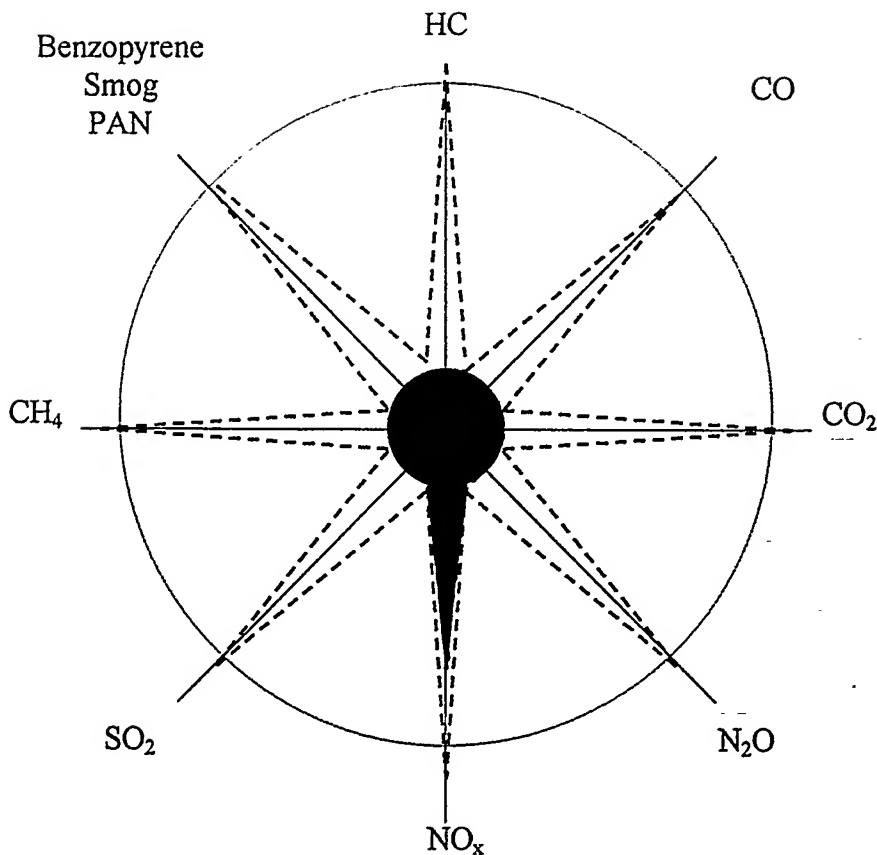


Figure 5.3 *Pollutants from a hydrogen fuelled motor vehicle*

In the diagram in figure 5.3, it is also possible to see that the only pollutants are oxides of nitrogen (both NO and NO_x).

Each one of the five criteria proposed in chapter 2.2.2 will be studied to investigate whether they are fulfilled or not.

A. Non renewable resources

It is possible to produce hydrogen from only renewable resources, though, today, most of the production is based on the use of fossil fuels.

It is neither necessary to use fossil fuels in the storage or distribution of hydrogen.

The criteria is fulfilled.

B. Ozone layer

NO_x is an important factor both for the depletion of the stratospheric ozone layer, and for the tropospheric ozone layer increasing. Since the hydrogen combustion give rise to emissions of NO_x, the criteria is not fulfilled. However there is no dispersion of HC, CO or N₂O.

The amount of NO_x is much lower than the one from gasoline (possible as much as 60 % less [5]). This, combined with the fact that we have no dispersion of HC and CO, makes hydrogen a better alternative than gasoline, and the criteria is almost fulfilled.

C. Greenhouse effect

There is no dispersion of CO_2 , the primary greenhouse gas. Further on, the other substances that contributes to the greenhouse effect, CO and N_2O , do not exist in the combustion process.

The criteria is fulfilled without any demarcations.

D. Acidification

Since there is no sign of emissions of CO_2 and SO_2 , the only pollutant to consider here is yet again NO_x . As mentioned before, the dispersion is low compared with gasoline.

The criteria is not fulfilled, but as in criteria B almost fulfilled, and considered to be a better alternative than gasoline.

E. Toxic substances

There are no toxic pollutants like PAN, benzopyrene, CO and SO_2 , or waste products from the utilisation of hydrogen. But hydrogen is classified as fire and explosive hazardous.

The criteria can be considered to be fulfilled.

5.3 Characterisation of Methanol

Combustion of methanol results in emissions of HC, CO, CO_2 and NO_x .

In table 5.4, the values for the emissions are shown.

	Passenger car driven by methanol produced from biomass
NO_x	0.123
HC	0.054
CO	3.035
CO_2	0.108

Table 5.2 Exhaust values (g/km) for a passenger car, where the fuel is methanol produced from biomass [21]

Figure 5.4 shows the diagram for a methanol fuelled motor vehicle.

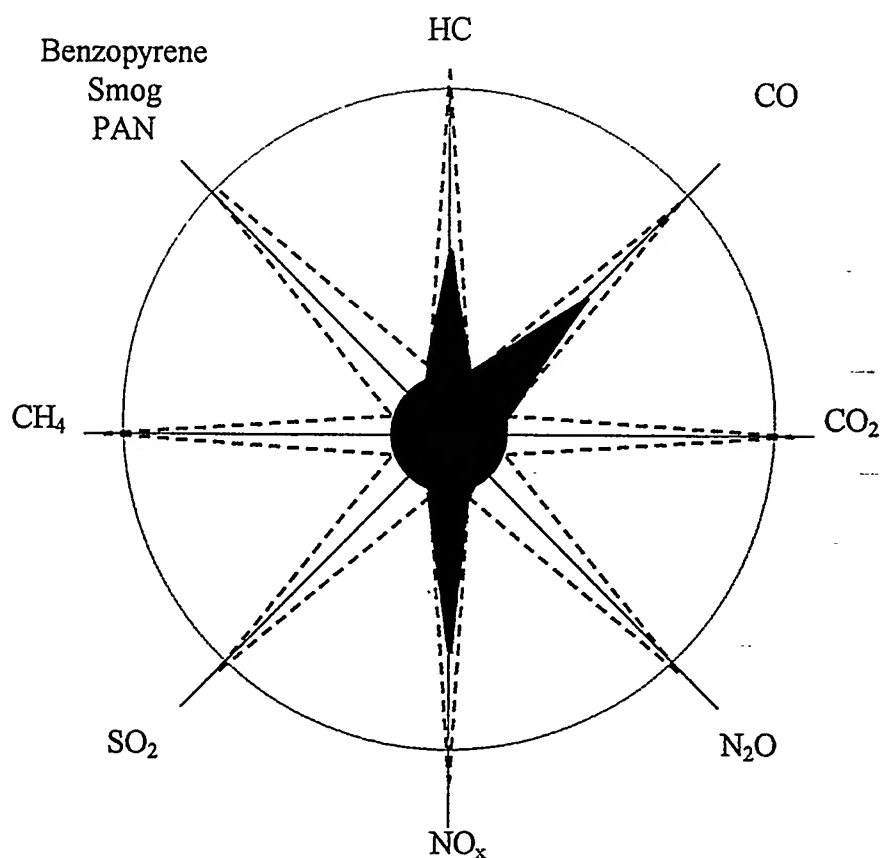


Figure 5.4 Pollutants from a methanol fuelled motor vehicle

We will have a closer look at the different criteria to see if they are fulfilled or not.

A. Non renewable resources

Methanol can be produced without any involvement of fossil fuels.

The criteria is fulfilled.

B. Ozone layer

Here, the stratospheric ozone layer is affected negatively by HC, CO and NO_x. Since NO_x is a product from the methanol combustion, the tropospheric ozone layer will also increase.

However, compared with gasoline combustion it can be observed that the discharge of these substances are all lower for methanol combustion.

Emissions of HC is only about half of what is obtained from a gasoline vehicle, and CO reaches up to 60 % of those from gasoline.

Hence, the criteria concerning the ozone layer is not fulfilled, but the choice of methanol can be considered as a better alternative than gasoline.

C. Greenhouse effect

The dispersion of CO₂ given by methanol, can be kept at desirable, constant level, by the ecological system, if methanol is produced from renewable resources like wood fuels.

The criteria is fulfilled.

D. Acidification

There are no emissions of SO₂. The NO_x emissions existing does not reach the same high rate as for gasoline combustion. This makes methanol a better alternative than gasoline.

The criteria is not fulfilled.

E. Toxic Substances

Methanol is classified as a toxic substance, which contributes to the formation of formaldehydes, aldehydes and CO.

The criteria is not fulfilled.

5.4 Result of the Comparison

To make the characterisation of hydrogen complete, it is necessary to compare them with gasoline. Table 5.5 shows a summarisation of the result of the characterisation compared with gasoline.

	Criteria concerning	Hydrogen	Methanol	Gasoline
A.	Renewable resources	Yes	Yes	No
B.	Ozone layer	No ¹	No ¹	No
C.	Greenhouse effect	Yes	Yes	No
D.	Acidification	No ¹	No ¹	No
E.	Toxic substances	Yes	No	No

¹Can be considered to be a better alternative compared with gasoline, due to lower dispersion of the listed emissions

Table 5.5 *Comparison between the different fuels*

As can be seen, hydrogen fulfil 3 of 5 of the criteria, and should therefore be considered to be the best alternative. Even those criteria which hydrogen does not fulfil, it can still be

considered as a better option compared with gasoline. It might even be possible to say that hydrogen is better than gasoline in all the areas treated in this investigation.

Methanol fulfil 2 of 5 of the criteria, and is therefore not considered to be as good as hydrogen in this comparison, but still much better compared with gasoline. But, there is of course also a lot of other things to consider, like for instance economy and safety, where another result may occur.

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